SURFACE MODIFICATION OF MATERIALS USING AN EXTREMELY NON-EQUILIBRIUM OXYGEN PLASMA

MODIFIKACIJA POVRŠINE MATERIALOV Z IZRAZITO NERAVNOVESNO KISIKOVO PLAZMO

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Several technological processes based on the interaction of extremely non-equilibrium oxygen plasma are described. A plasma with a low kinetic temperature of heavy particles and an extremely high density of neutral oxygen atoms is created in glass plasma reactors by inductively coupled radio-frequency (RF) discharges. The density of the charged particles is kept low at around 10^{16} m^{-3}, while the density of the neutral oxygen atoms may exceed a value of 1×10^{22} m^{-3}. The neutral oxygen atoms are chemically active and readily react with solid materials, even at low temperatures. The interaction of the oxygen atoms with metal samples often causes a rapid nucleation of metal oxide isles and the spontaneous growth of one- or two-dimensional structures, such as nanowires and nanobelts. These "nanofeatures" are often monocrystalline. The exposure of different carbon-rich materials to an oxygen plasma is applied for the functionalization with oxygen functional groups as well as for the controlled oxidation of various materials. The superhydrophilicity of several polymers and composites can be achieved. The technique is suitable for the destruction of bacteria and thus the sterilization of delicate materials.

Keywords: plasma, oxygen, metal oxide nanoparticles, polymer functionalization, sterilization

Opisani so nekateri tehnološki postopki za obdelavo materialov z izrazito neravnovesno kisikovo plazmo. Stanje plinske plazme z nizko kinetično energijo težkih delcev in zelo veliko gostoto nevtralnih kisikovih atomov se vzpostavi v induktivno sklopljeni radiofrekvenčni plinski razelektritvi v steklenem plazemskem reaktorju. Gostota nabitih delcev v takšni plazmi je razmeroma majhna in navadno ne presega vrednosti 1×10^{16} m^{-3}, medtem ko lahko gostota nevtralnih kisikovih atomov preseže vrednost 1×10^{22} m^{-3}. Nevtralni kisikovi atomi so kemijsko izredno aktivni in reagirajo s površino trdnih snovi že pri nizki temperaturi. Interakcija kisikovih atomov s površino kovinskih materialov pogosto povzroči bliskovito nukleacijo otočkov kovinskega oksida, iz katerih spontano rastejo eno- ali dvodimenzionalne strukture, kot so nanožice in nanotrakovi. Nanomateriali so pogosto monokristalinični. Materiali, ki vsebujejo ogljik, prav tako reagirajo z atomskim kisikom. Že majhna doza atomov povzroči modifikacijo površine tovrstnih materialov z nastankom kisikovih funkcionalnih skupin. Tako obdelani polimerni materiali so včasih superhidrofilni. Podaljšana izpostava organskih materialov kisikovim atomom vodi k postopni oksidaciji in s tem počasnemu jedkanju materialov. Pojav izkoriščamo pri sterilizaciji občutljivih organskih materialov, ki ne prenesejo klasičnih postopkov.

Ključne besede: plazma, kisik, nanodelci kovinskega oksida, funkcionalizacija polimerov, sterilizacija

1 INTRODUCTION

The increasing demands on the quality as well as the miniaturization of products facilitate the development of new technological processes. These new technologies should ensure the good quality of products, low production costs and should be environmentally acceptable. Classical approaches to the treatment of materials have been almost exhausted and industry is looking for new ideas. The majority of breakthrough technologies that have appeared in recent years are based on the application of non-equilibrium environments, especially non-equilibrium gaseous plasma.[1] A variety of gases are used to create a plasma with suitable properties[1]. A plasma of particular interest is created with oxygen[1]. Molecular oxygen is passed through an electrical discharge. The fast electrons then excite the neutral molecules with the original Maxwell-Boltzmann (MB) distribution causing a dramatic shift to the non-equilibrium state. Apart from neutral molecules in low ro-vibrational states, substantial amounts of highly excited molecules, neutral atoms and ionized molecules and atoms are created.[2–3] While the distribution of neutral molecules over translational states is preserved close to MB due to the poor kinetic energy exchange between fast electrons and slow neutrals during elastic collisions, it is not true for internal energy distribution. Two excited states of molecular oxygen are metastable (at the excitation energy of approximately 1 eV and 2 eV) and their concentration is far above the values calculated using MB distribution at room temperature.[4] Furthermore, the dissociation degree is far from the equilibrium value and the same applies for the ionization fractions. Different temperatures that are suitable for a description of such a non-equilibrium state of oxygen depend on the particular conditions (discharge and plasma parameters).[5] The largest shift from MB distribution is often observed by passing the oxygen through the radio frequency of microwave discharges created in glass plasma reactors. At the neutral gas kinetic temperature close to room temperature, the other temperatures (T) are as follows: vibrational temperature 500–1000 K, dissociation temperature 100 000 K or even higher, ionization temperature 10 000–50 000 K, electron temperature

15 000–50 000 K.[6] Such a non-equilibrium gas often acts as an ordinary gas at room or slightly elevated temperature in terms of the heat dissipation on solid materials, while it acts as an extremely hot gas (well over 10,000 K) in terms of chemical activity. Obviously, heavily non-equilibrium oxygen is used for the rapid chemical modification of solid materials at low temperature.[7]

2 DETERMINATION OF THE KEY PLASMA PARAMETERS

Plasma is a partially ionized gas, and the most obvious plasma parameters are the density of the charged particles (free electrons and positive ions) and their temperatures (or the kinetic energy distribution functions in the case the particles that are away from the MB distribution). Apart from these, another couple of parameters are often stated, i.e., the plasma potential (V_s) and the Debye length (λ_D). In many cases, both are calculated with equations:[8]

$$V_s - V_f = \frac{-kT_e}{2e_0} \ln \frac{m_+}{2m_e} \qquad (1)$$

and

$$\lambda_s = \sqrt{\frac{kT_e}{N_e e_0^2}} \qquad (2)$$

In equations (1) and (2), V_s is the plasma potential (often called the space potential), V_f is the floating potential, e_0 is the elementary charge, k is the Boltzmann constant, T_e is the electron temperature, m_+ is the positive ion mass, m_e is the electron mass, N_e is the electron density, and ε_0 is the vacuum permittivity. These two equations are useful only as long as some requirements are fulfilled. Obviously, one requirement is the MB distribution of electrons. The set of parameters T_e, N_e, V_s, λ_D is useful for describing the electrical properties of the plasma, but tell little about its chemical reactivity. Apart from these classical parameters, many others are necessary for a decent characterization of the processing plasma, and they include the rotational and vibrational temperature of the neutral and charged molecules, the density of the neutral atoms, the density of the metastable molecules and atoms, and the ionization fractions of the molecules and atoms. In a plasma of electronegative gases, the density of the negatively charged heavy particles is not negligible, either. Complete plasma characterization is obviously a difficult task, so numerous methods have been developed and applied more or less successfully. Among them, electrical, magnetic and catalytic probes[9–18] are worth mentioning, along with more complicated techniques, such as a variety of optical emission[19–21] and absorption techniques,[22] the propagation of electromagnetic waves,[6] and chemical titrations.[23] A proper determination of the parameters is crucial for a calculation of the fluxes of the reactive plasma particles on the surface of the samples as well as the kinetic energy of the charged particles interacting with plasma facing materials. Although modern plasma laboratories are well equipped with several different tools, plasma is often characterized insufficiently.

3 SINTHESIS OF METAL OXIDE NANOPARTICLES

A novel technology based on the application of non-equilibrium oxygen plasma is the synthesis of large quantities of metal oxide nanoparticles.[24–32] Metallic foils are exposed to oxygen plasma with a dissociation fraction of the order of 10 % (corresponding to a dissociation temperature of 22 500 K).[24] Neutral oxygen atoms are, by far, more reactive than their parent molecules and interact with the surface of solid materials both chemically and physically. Chemical reactivity causes the formation of metal oxides, while the physical interaction is predominantly demonstrated by the accommodation (relaxation) of metastable molecules and the heterogeneous surface recombination of neutral oxygen atoms.[33–34] Furthermore, the bombardment of the metal surface with positive ions from the plasma is observed as well as the neutralization of charged particles. All the chemical and physical reactions are heavily exothermic, causing a localized disturbance of the surface atoms from their (quasi)equilibrium positions. The surface atoms become extremely mobile, so a disturbance of the crystalline structure occurs.[35–37] The extremely high mobility of the surface atoms allows for the creation of (meta)stable chains of metal oxides, stretching perpendicularly from the surface plain, as shown by molecular dynamics simulations.[38] An example of such a chain is shown in **Figure 1**. The chains act as nuclei for the growing of nanofeatures from the surface of the metal samples. As long as the mobility of the surface atoms is much higher in the preferred direction than in other orientations, the growth is one-dimensional, resulting in
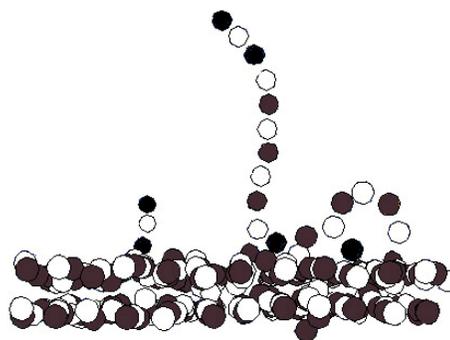

Figure 1: The results of a molecular dynamics simulation of the interaction of oxygen atoms added to the surface of nickel foil. The figure shows the formation of NiO chains. Dark and white particles stand for the O and Ni atoms, respectively.
Slika 1: Rezultati simulacije molekulske dinamike interakcije kisikovih atomov na površini nikljeve folije. Slika prikazuje tvorjenje verig NiO. Temni krogci prikazujejo kisikove atome, beli pa nikljeve.
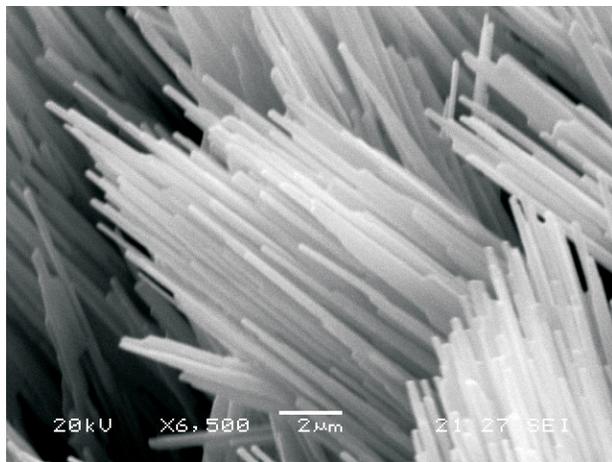
Figure 2: Nanowires of niobium pentoxide stretching from the surface of a niobium foil during exposure to an extremely non-equilibrium oxygen plasma with the following parameters: a neutral gas kinetic temperature of about 500 K, an electron temperature of 20 000 K, an ionization fraction of about 1×10^{-6} and a dissociation fraction of about 13 %.

Slika 2: Nanožičke niobijevega pentoksida, rastoče na površini niobijeve folije med izpostavo neravnovesni kisikovi plazmi z naslednjimi parametri: temperatura nevtralnega plina okoli 500 K, temperatura elektronov 20 000 K, delež ionizacije okoli 1×10^{-6} in delež disociacije okoli 13 %

long nanowires rather than other forms. **Figure 2** represents a SEM image of such nanowires, growing from the surface of niobium foil exposed to an extremely large flux of oxygen atoms of close to $1 \times 10^{24} \text{ m}^{-2} \text{ s}^{-1}$.[24] It is assumed that the nanowires are monocrystalline Nb_2O_5, the most stable form of niobium oxide. In the case of a lower dissociation fraction (lower O flux at
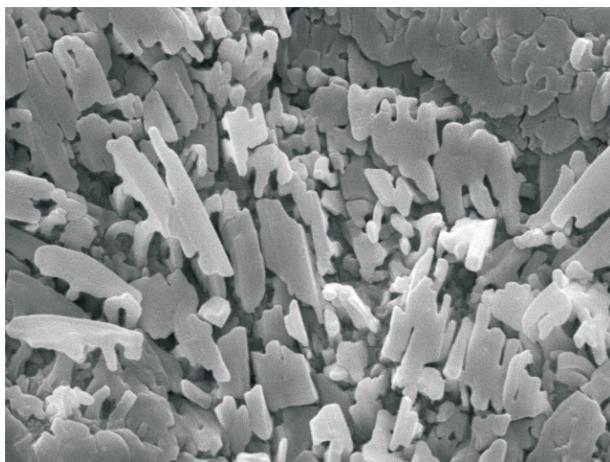

Figure 3: Rectangular nanoparticles of niobium pentoxide growing from the surface of niobium foil during exposure to highly non-equilibrium oxygen plasma with the following parameters: a neutral gas kinetic temperature of about 500 K, an electron temperature of 20 000 K, an ionization fraction of about 8×10^{-7} and a dissociation fraction of about 4 %.

Slika 3: Pravokotni nanodelci niobijevega pentoksida, rastoči na površini niobijeve folije med izpostavo neravnovesni kisikovi plazmi z naslednjimi parametri: temperatura nevtralnega plina okoli 500 K, temperatura elektronov 20 000 K, delež ionizacije okoli 8×10^{-7} in delež disociacije okoli 4 %.

about $3 \times 10^{23} \text{ m}^{-2} \text{ s}^{-1}$), other features grow from the surface of the metal foils. **Figure 3** shows nanobelts of rectangular shape growing from the surface of the niobium foils. Fluxes below about $1 \times 10^{23} \text{ m}^{-2} \text{ s}^{-1}$ do not produce such interesting nanoparticles. Namely, at a low flux, the surface mobility of the atoms is too low to allow for the rapid growth of one- or two-dimensional structures, so the oxidation mechanism is close to that characteristic for a thermal (equilibrium) treatment. Similar results are obtained with many other metals, including Fe, V, Mo, Cr.[29]

4 SURFACE ACTIVATION OF POLYMER MATERIALS

A popular application of oxygen plasma is the surface functionalization of organic materials.[39–56] Polymer materials are usually hydrophobic with a fairly low surface energy. This hydrophobicity is usually the consequence of a poor concentration of polar functional groups on the surface of the polymers. In thermal equilibrium the concentration of the functional groups on the surface is the same as the bulk concentration. The surface properties of polymer materials are changed by the incorporation of different functional groups on the very surface.[39–40,50–51,54–55] Obviously, the new surface functional groups are not very stable and tend to decay spontaneously.[47] Several techniques for the functionalization of organic materials have appeared. Since the presence of foreign functional groups on the surface is not thermodynamically favorable, the obvious technique is the application of a non-equilibrium gaseous plasma. As mentioned above, non-equilibrium oxygen plasma with the kinetic temperature close to room temperature acts as an almost perfect medium for the surface functionalization with oxygen functional groups. Its extreme chemical reactivity allows for rapid functionalization at minimal thermal loading.[43] The applicability of this technology is demonstrated for the case of industrial LDPE (low-density polyethylene) polymer foil used for packaging (**Figures 4** and **5**).[57] The polymer is exposed to oxygen plasma at almost room neutral gas kinetic temperature, a dissociation fraction of about 10 % and a rather low ionization fraction of 1×10^{-6} (corresponding to the ionization temperature of about 12 000 K). The material heating due to the surface neutralization of charged particles is therefore negligible. Furthermore, the Debye length in such plasma is much larger than the mean free path of oxygen molecules or atoms. Therefore, the kinetic energy that the ions gain passing the potential difference between space and floating potentials (see equation (1)) is effectively distributed to neutral molecules or atoms before colliding with the polymer surface. The polymer material is therefore the subject of extremely poor heating, but high chemical modifications. Assuming an infinite planar geometry, the flux of ions (j_+) and atoms (j_a)
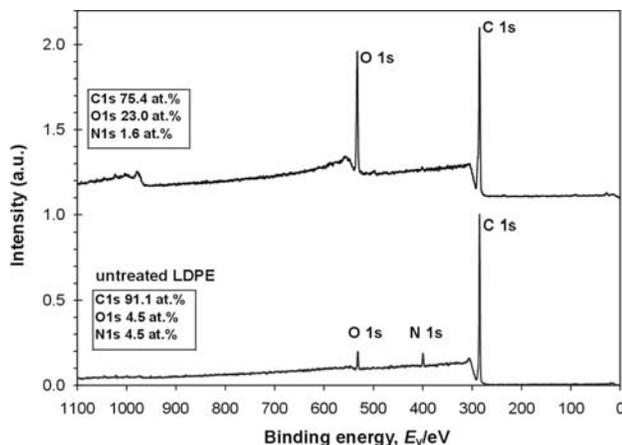
Figure 4: The XPS (X-ray photoelectron spectroscopy) survey spectra of untreated and plasma-treated industrial LDPE polymer foil. The oxygen concentration in the surface film of the polymer is increased to 23 % after treatment with plasma with the following parameters: a neutral gas kinetic temperature of about 400 K, an electron temperature of 20 000 K, an ionization fraction of about 1×10^{-6} and a dissociation fraction of about 10 %. The treatment time was 3 s.
Slika 4: Pregledni spekter XPS (rentgenske fotoelektronske spektroskopije) neobdelane in plazemsko obdelane polimerne folije LDPE. Koncentracija kisika na površini polimera je narasla na 23 % po obdelavi s plazmo z naslednjimi parametri: temperatura nevtralnega plina okoli 400 K, temperatura elektronov 20 000 K, delež ionizacije okoli 1×10^{-6} in delež disociacije okoli 10 %. Čas obdelave je bil 3 s.

onto the surface of the polymer does not depend on sheath properties, and is as follows:[58]

$$j_+ = ¼\, n_+ <v_+> \tag{3}$$

$$j_a = ¼\, n_a <v_a> \tag{4}$$

Here, n_+ is the density of positively charged ions, $<v_+>$ is the average absolute random velocity of positively charged ions assuming an MB distribution, n_a is the neutral atom density, and $<v_a>$ is the average absolute random velocity of neutral oxygen atoms, assuming an MB distribution.
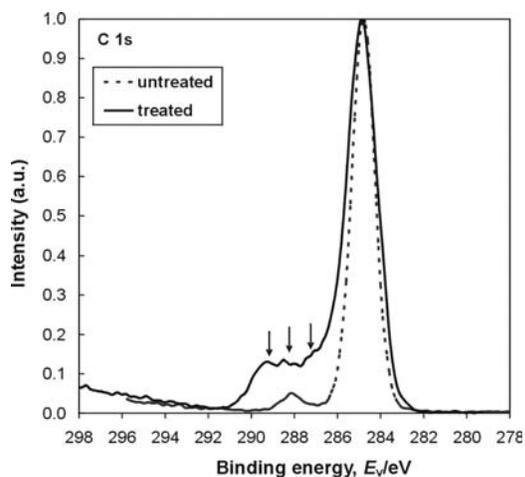

Figure 5. High-resolution C1s XPS peak for industrial LDPE polymer foil treated undert same conditions as in **Figure 4**
Slika 5: Visoko ločljivi spekter XPS vrha C1s industrijske polimerne folije LDPE, obdelane pri istih pogojih kot na **sliki 4**

There are few reasons for the acceleration of heavy charged particles (molecular and atomic ions) in high-frequency discharges. Namely, as the frequency of the electrical field approaches a few MHz, the local electromagnetic oscillations become too fast to be followed by heavy particles. Only the electrons can be heated (can gain kinetic energy) in radio-frequency fields. The distribution of heavy charged particles over translational states is thus the same as those for neutral particles – MB close to room temperature. The average velocity of the positively charged ions in equation (3) is therefore the same as for the neutral particles at room temperature (*T*): $<v_+>$ = 440 m/s for molecular ions and 630 m/s for atomic ions. The average velocity was calculated from equation $v = \sqrt{8kT/\pi m}$, where k is the Boltzmann constant and m is the ion mass.[58] Since the density of the molecules in the plasma is an order of magnitude larger than the density of the atoms, and since the dissociative ionization is energetically less favorable than the ordinary ionization of the molecules, the contribution of atomic ions is easily neglected and $<v_+>$ can be approximated to the value characteristic for molecules, i.e., 440 m/s. The resultant flux of ions (j_+) on the polymer surface exposed to plasma is thus:[58]

$$j_+ = ¼\, n_+ <v_+> = ¼\, 3 \times 10^{16}\ \text{m}^{-3} \times 440\ \text{m/s} =$$
$$= 3.3 \times 10^{18}\ \text{m}^{-2}\text{s}^{-1} \tag{5}$$

Ions are recombined on the surfaces of all solid materials at a very high rate, close to 100 %. The thermal load per unit area caused by ion recombination is:[42]

$$P_+ = j_+\, W_i = 3.3 \times 10^{18}\ \text{m}^{-2}\text{s}^{-1} \times 12 \times 1.6 \times 10^{-19}\ \text{J} =$$
$$= 6\ \text{W m}^{-2} \tag{6}$$

Here, P_+ is the power dissipated by the oxygen ion recombination per unit area and W_i is the ionization energy of the oxygen molecules, i.e., about 12 eV. The power P_+ is extremely low, so heating by ions is always negligible, as long as the ionization fraction is that low. The upper calculation is valid for the case when oxygen molecular ions are found in the ground state. In practice, this is never completely true, since there are always some excited ions in oxygen plasma. Fortunately, the density of ions with a high excitation energy in plasma with a low ionization fraction and a rather low electron temperature is usually negligible, so the upper calculation is a good approximation. The positive ions are accelerated in the sheath between the plasma and the surface (according to equation (1)) so the heating by ions is larger than the value given by (6). The maximum heating is obviously in the case of collision-less sheath when the ions gain a kinetic energy of $e_0 (V_s - V_f)$[8]. As explained above, however, the ions lose their kinetic energy in the gas phase as long as the Debye length is much larger than the mean free path of the molecules.

The heating of polymer materials by the recombination of neutral atoms is often also negligible. The thermal load per unit area due to this effect is calculated taking into account equation (4):[59]

$$P_a = 1/4 \; n_a <v_a> \gamma \; W_D/2 = 1/4 \times 6 \times 10^{20} \text{ m}^{-3} \times$$
$$\times \; 630 \text{ m s}^{-1} \times 10^{-4} \times 5.2 \times 1.6 \times 10^{-19} \text{ J} / 2 = 4 \text{ W m}^{-2} \quad (7)$$

Here, γ is the recombination coefficient and W_D is the dissociation energy, i.e., $W_D = 5.2$ eV. The recombination coefficient for flat polymer materials is low, often of the order of 10^{-4}. Taking into account this value, the power dissipated on the polymer surface due to the recombination of atoms is approximately $P_a = 4$ W m^{-2}. The total contributions of the neutral atom recombination (P_a) and the neutralization of ions (P_+) are $P = P_a + P_+$ and are therefore about 10 W m^{-2}. A polymer foil with a thickness d of 10 μm is therefore heated at:[58]

$$dT/dt = P/(\rho \; c_p \; d) = 10 \text{ W m}^{-2} / (10^3 \text{ kg m}^{-3} \times$$
$$\times \; 1 \text{ kJ kg}^{-1} \text{ K}^{-1} \times 10 \times 10^{-6} \text{ m}) = 1 \text{ K/s} \quad (8)$$

This value, of course, depends on the properties of a particular polymer (the density ρ and the thermal capacity c_p) and is only a rough estimation. It depends also on the surface roughness (rough materials are heated at a faster rate) and the thickness (thicker materials are heated at lower rates). Since the flux of atoms on the surface is enormous (in the above calculation the value of 1×10^{23} m^{-2} s^{-1} was taken into account), the surface of the polymer is saturated with oxygen functional groups in much less than a second, so far before any substantial heating of the material occurs.

5 STERILIZATION OF DELICATE MATERIALS

Since plasma treatment does not heat the materials much, oxygen plasma is used for the sterilization of delicate biocompatible materials.[60–65] Namely, oxygen plasma interacts with bacteria already at room temperature, causing the destruction of the bacterial cell wall and, therefore, sterilization. The sterilization effect is illustrated by **Figures 6** and **7**. **Figure 6** is an SEM image of the live bacterium *Bacillus Stearothermophilus*. The bacteria were deposited on substrates and treated with oxygen plasma with a neutral gas kinetic tempera-
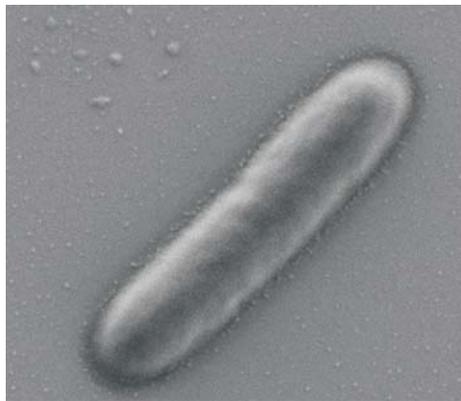
ture of about 400 K, an electron temperature of 20 000 K, an ionization fraction of about 3×10^{-6} and a dissociation fraction of about 10 %.[62] The effect of the plasma treatment is well illustrated by **Figure 7**. The treatment time was 55 s. The reactive particles from the oxygen plasma (mainly neutral oxygen atoms) readily reacted with the bacteria. The capsule protecting the live bacteria disappeared and the bacterial cell wall is badly damaged. What remains from the bacteria after the plasma treatment is just the remnants of the bacterial cytoplasm. Obviously, some parts of the cytoplasm do not react with the plasma particles as much as the bacterial cell wall, let alone the capsule. The type of bacteria was not chosen accidentally. Bacteria *Bacillus Stearothermophilus* is famous for its resistance to prolonged heating at elevated temperature.[66] Even a half an hour treatment at 100 °C is not sufficient to ensure the sterility of objects contaminated with this type of bacteria. Plasma sterilization is therefore a promising method for the destruction of bacteria on biocompatible objects that do not stand standard autoclaving in humid air at 130 °C. Since the bacterium presented in **Figure 7** is very badly damaged it can be concluded that plasma treatment times shorter than a minute are sufficient for the sterilization by extremely non equilibrium oxygen plasma.

6 CONCLUSIONS

Some applications of extremely non-equilibrium oxygen plasma were presented. An oxygen plasma with a high degree of dissociation is created in a radio-frequency discharge. The neutral gas kinetic temperature remains close to room temperature, so the thermal loads on substrates are minimal. The chemical reactivity of such plasma, on the other hand, is extremely high. Such plasma is suitable for the modification of both inorganic and organic materials. The exposure of metal foils leads to the spontaneous growth of metal oxide nanoparticles.
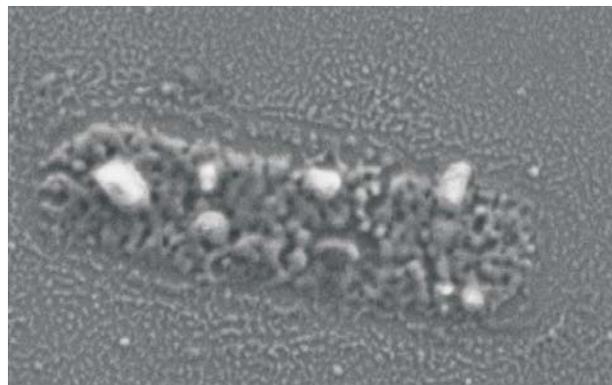

Figure 6: SEM image of *Bacillus Stearothermophilus* before plasma treatment
Slika 6: SEM slika bakterije *Bacillus Stearothermophilus* pred pla-zemsko obdelavo

Figure 7: SEM image of *Bacillus Stearothermophilus* after treatment with plasma for 55 s. The plasma parameters were the same as for the treatment of the polymer foil (as in **Figure 4**).
Slika 7: SEM slika bakterije *Bacillus Stearothermophilus* po obdelavi v plazmi 55 s. Parametri plazme so bili isti kot pri obdelavi polimerne folije (kot na **sliki 4**).

As long as the flux of atoms on the surface of the samples is very large, an oxide film will grow in the form of long nanowires. At moderate flux, the oxide is often in the form of rectangular nanoparticles. The treatment of polymer materials with an oxygen plasma leads to a surface functionalization with oxygen-rich functional groups. Even a brief exposure results in a saturation of the surface with polar functional groups, causing a dramatic increase in the surface energy and thus the wettability. Treatment with oxygen plasma also causes the destruction of bacteria and therefore represents a suitable medium for the sterilization of delicate biocompatible objects.

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