

INTERACTION OF HIGHLY DISSOCIATED OXYGEN PLASMA WITH POLYMERS AND THEIR COMPOSITES

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Abstract: Recent application of fully dissociated oxygen plasmas with a low density of charged particles for treatment of polymers and polymer-matrix composite materials is described. Plasma is often created in a high frequency inductively coupled discharge to avoid ion acceleration. At the pressure of few mbar the plasma density is often of the order of 10^{16} m^{-3} , and the density of neutral oxygen atoms of the order of 10^{21} m^{-3} . The dissociation fraction of oxygen molecules may approach 100%. Plasma with such characteristics causes modification of solid materials. It is extensively used for surface cleaning and activation, selective etching and sterilization. The first effect of plasma treatment is surface activation. The wettability of materials is increased dramatically enabling their painting, printing and metallization. The treatment time depends on the type of materials and plasma parameters. Optimal wettability is often obtained in less than 1 s of plasma treatment thus making the technology suitable for industrial use. Prolonged plasma treatment of polymer matrix composites causes selective etching. Different components are etched at different rates. The highest is the etching rate of the polymer matrix, while inorganic fillings are not etched at all. Oxygen plasma treatment of the composites thus represents a unique method for studying the distribution as well as the orientation of different fillings in composites. The application of this technology is illustrated with several examples.

Interakcija visoko disociirane kisikove plazme s polimeri in njihovimi kompoziti

Ključne besede: Kisikova plazma, Kompozit, Polimer, Prevleka, Porazdelitev delcev, Analiza slik, Preiskava površin

Izvleček: V prispevku je opisana uporabnost nizkotlačne popolnoma disociirane kisikove plazme za obdelavo polimerov in kompozitnih materialov s polimerno matriko. Takšno plazmo pogosto generiramo v visokofrekvenčni induktivno sklopljeni razelektritvi, s čimer se izognemo pospeševanju ionov v električnem polju. Pri tlaku nekaj mbar je gostota plazme reda velikosti 10^{16} m^{-3} , gostota nevtralnih kisikovih atomov pa reda 10^{21} m^{-3} . Stopnja disociiranosti kisikovih molekul se lahko približa 100%. Plazma s tovrstnimi značilnostmi povzroča spremembo trdnih materialov in se široko uporablja za čiščenje, aktivacijo, selektivno jedkanje in sterilizacijo. Prvi pojav, ki ga opazimo pri izpostavi trdnih materialov kisikovi plazmi, je površinska aktivacija. Omočljivost tako obdelanih materialov se dramatično poveča, kar omogoča dober oprijem materiala pri barvanju, tiskanju in metalizaciji. Značilni čas obdelave je odvisen od vrste materiala in plazemskih parametrov. Optimalno omočljivost pogosto dosežemo že v času, manjšem od 1 s, kar omogoča industrijsko uporabo. Podaljšana plazemska obdelava kompozitov s polimerno matriko vodi k selektivnemu jedkanju. Različne komponente v kompozitu se jedkajo z različno hitrostjo. Največja je hitrost jedkanja polimerne matrike, medtem ko se anorganska polnila sploh ne jedkajo. Plazemska obdelava kompozitov tako predstavlja edinstveno metodo za preiskavo porazdelitve in celo orientacije polnil v kompozitih. Aplikacija te tehnologije je ilustriрана z različnimi primeri.

1 Introduction

In the past decade, oxygen plasma has been successfully applied to novel technologies such as plasma ashing, plasma cleaning, selective plasma etching and plasma sterilization [1-18]. All the technologies are based on controlled oxidation of organic compounds. In contrary to standard oxidation that is carried on close to the thermodynamic equilibrium, the oxidation in plasma is a well non-equilibrium process. The main advantage of the non-equilibrium oxidation is the capability of controlling the oxidation rate independently from the sample temperature. This is possible due to a low potential barrier for oxidation with reactive particles from oxygen plasma. Oxygen plasma is a source of different reactive particles including excited molecules and atoms, positive and negative molecular and atomic ions, ozone and neutral oxygen atoms. The concentration of these particles depends largely on discharge parameters (i.e. type of discharge, discharge power and frequency, magnetic field, size and shape of discharge vessel, type of material facing plasma, pressure and gas mixture, etc.) Interaction of plasma radicals with solid materials is both

physical and chemical. Physical interaction is usually performed with charged radicals that can be accelerated by biasing samples, while neutral radicals usually do not have substantial kinetic energy so the interaction is purely potential and therefore very selective. Optimal oxidation selectivity is therefore obtained with plasma of low ion density and high neutral radical density.

2 Inductively coupled RF oxygen plasma

Plasma is usually created in a gaseous discharge. Electrons are accelerated in electric field and thermalized at elastic collisions. Their energy distribution function is therefore rather Maxwellian with the temperature of several eV. Electrons in the high-energy tail of the distribution function have enough energy for direct ionisation of gaseous molecules, while those in the low energy part of the distribution function are only capable to excite rotational and vibrational excited states of molecules. In the case of oxygen molecules, the excitation energy for ro-vibrational states is well

below 1 eV, the excitation energy for metastable molecules $O_2^1\Delta$ and $O_2^1\Sigma$ is about 1 and 2 eV, respectively, the dissociation energy is 5.2 eV, while the ionisation energy is 12 eV. Electrons with the average energy of few eV are therefore likely to excite molecules into metastable states and ro-vibrational states, while dissociation and ionisation is less probable.

Excited particles tend to de-excite. There are many channels for de-excitation, some of them occur in the gas phase, while the others take place on the surface of the discharge chamber. In any case, the conservation of energy and momentum as well as rules of quantum mechanics should be obeyed. Vibrationally excited states are de-excited in the gas phase primarily by vibration interchanges (V-V transitions) and super-elastic collisions with atoms (V-T transitions) [8]. Neutral oxygen atoms in the ground state can recombine to molecules only at three-body collisions that are unlikely to occur at low pressure (say below few mbar) so they are rather stable in the gas phase.

Surface de-excitations often play a dominant role in low-pressure plasmas. The probability for ion recombination as well as metastables relaxation is close to unity [19], while the recombination of neutral oxygen atoms depends largely on the type of material facing plasma as well as its temperature and morphology. The probability for recombination at heterogeneous surface recombination ($O + O \rightarrow O_2$) for many glasses and some ceramics is often low (the typical order of magnitude in 10^{-4}), while for many metals and some porous ceramics it is of the order of 10^{-1} . The recombination probability does not depend only on the type of material, but also on other parameters.

At low flux of oxygen atoms onto the surface, the recombination probability depends on the surface coverage with O atoms. This phenomenon was often observed at high vacuum, when the flux of O atoms onto the surface is below say $10^{22} \text{ m}^{-2}\text{s}^{-1}$. When the flux is increased, the surface becomes saturated with O atoms and the recombination probability approaches a constant value, that has been known as the recombination coefficient (γ). The recombination coefficients depend on the material, the surface morphology, and often also on the temperature. There seems to be no general rule, but the recombination coefficient tends to increase with increasing surface roughness as well as increasing surface temperature.

The density of different excited species in plasma depends on excitation and de-excitation probabilities. The excitation probabilities depend mostly on electron density and temperature, while the de-excitation probabilities depend particularly on surface properties. By choosing smooth materials with low recombination coefficients for recombination of O atoms it is often possible to achieve plasma with a low density of ions but a high density of neutral atoms. It is often possible to obtain oxygen plasma with the ion density below 10^{16} m^{-3} and the neutral atom density above 10^{21} m^{-3} [20-23].

High oxidation selectivity can only be obtained with cold plasmas. Cold plasma is a state of gas with a low kinetic energy of heavy particles, i.e. all particles except electrons. There are some channels for heating heavy particles in plasmas. Happily enough, elastic collisions between fast electrons and heavy particles do not lead to substantial kinetic energy exchange due to a small mass of the electrons. The major channel for heating heavy particles at collisions with energetic electrons is a dissociation event. At direct electron impact dissociation, the excessive kinetic energy of the electron can be observed as the kinetic energy of newly formed atoms, which can move apart with a substantial kinetic energy. Such energetic atoms get effectively thermalized at elastic collisions with other heavy particles. A good way to avoid this sort of plasma heating is application of plasma with a rather low electron temperature.

Another mechanism of heating heavy particles is super-elastic collisions between vibrationally excited molecules and oxygen atoms. The reaction cross-section is large [19]. The only way to avoid such collisions is application of fully dissociated plasma where such collisions are unlikely to occur.

An important channel for heating heavy particles may be acceleration of ions in electric field. The ions are accelerated in electric field as are the electrons. As long as the electric field frequency is low, the ions can follow any change of the local electric field. The energy an oxygen ion can pick from the electric field is

$$W = (e^2 E^2) / (2m\omega^2). \quad (1)$$

Here, e is the ion charge, E peak electric field, m ion mass and ω electric field frequency. The kinetic energy an oxygen ion in a high vacuum can gain in electric field versus the frequency is plotted in Figure 1. As long as the frequency is low (say below 100 kHz), the ions are well accelerated in the field. But as the frequency is increased,

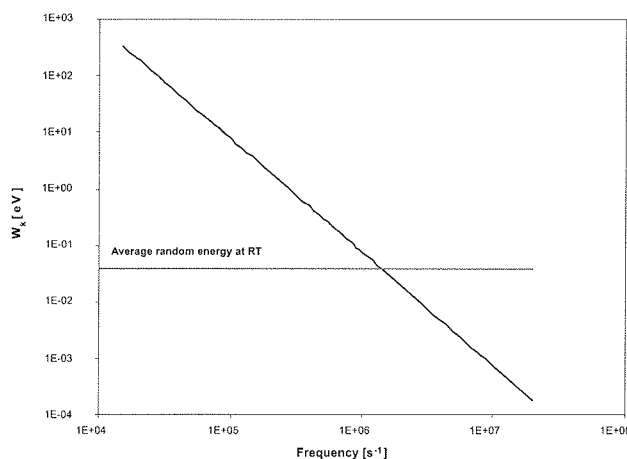


Fig. 1. Maximal kinetic energy of oxygen ions oscillating in a high frequency electric field of 100V/cm.

the ions are not able to follow the field. At the frequency of about few MHz, the kinetic energy an ion can pick from the field is less than average thermal energy of an ion at room temperature. This means that ions in the electric field with a frequency above 10 MHz cannot pick energy worth mentioning. As long as the electric field frequency is higher than 10 MHz, the ions thus cannot be accelerated in the field and cannot contribute to neutral gas heating.

Upper considerations lead to the conclusion that best oxygen plasma for selective oxidation of different materials is created in a radio-frequency discharge. A high degree of dissociation of oxygen molecules is obtained in a discharge chamber made from glass, which has a smooth surface and a low coefficient for recombination of oxygen atoms. There are two extreme modes for RF generator coupling: i) capacitive, and ii) inductive. In practice, the coupling is often a mixture of both extremes. Inductive coupling is often obtained using a coil wound around a glass tube. In this case, electrons are accelerated in induced electric field sustained due to alternating magnetic field in the coil. The electric field in the axis is rather low, and is increasing towards the edge of the glass tube.

Another extreme is capacitive coupling. In this case, the charged particles are accelerated in the alternating electric field between two parallel electrodes. A sheath with a substantial potential is established next to the powered electrode. As long as the sheath is almost collisionless (i.e. the mean free path is larger than the sheath thickness) the ions entering the sheath from the gas phase are accelerated towards the electrode and do not transfer kinetic energy to other particles. They bombard the electrode and some are reflected as neutral fast atoms or molecules. These fast particles do heat the neutral gas. The heat exchange between positive ions and other heavy particles is increased in the case the sheath is not collisionless. In such cases there are more channels for kinetic energy exchange in the gas phase. This often occurs at elevated pressure, say above 0.1 mbar, where the density of atoms increases with increasing pressure.

As the electric field frequency increases towards the microwave range, the ions can gain practically no energy from the field, and also electrons cannot pick as much energy as in the case of radio-frequency discharges. As a general rule, the electron temperature in simple microwave discharges is always lower than in radio-frequency discharges with comparable power. More energy is transferred to neutral gas heating so the microwave plasmas are never as cold as the RF plasmas.

3 Plasma parameters

Parameters of low pressure plasmas created by inductively coupled RF discharge in a glass tube depend on discharge power and pressure. Typical values are as follows: neutral gas kinetic temperature is often equal to ion kinetic temperature and is a bit more than room temperature - val-

ues between 300 and 500 K are common. The electron temperature is often about 50000 K or more. At the pressure of few 10 Pa, the density of electrons and ions is often between 10^{15} and 10^{16} m^{-3} , the density of neutral oxygen atoms of the order of 10^{21} m^{-3} while the density of metastable oxygen molecules of the order of 10^{19} m^{-3} . The plasma potential is often of the order of 10 V and the Debye length about 10^{-4} m . The density of neutral oxygen atoms is certainly the most important parameter.

Several methods have appeared to measure the O density in highly dissociated oxygen. The methods include optical spectroscopy /24-27/, mass spectrometry /28-29/, gas titration /22, 30/ and catalytic probes /31-42/. The latter was found to have some advantages over other techniques, as catalytic probes enable real/time measurements and do not disturb the original concentration of O atoms. The disadvantages include a poor understanding of surface recombination phenomena and sensitivity to high-frequency interferences. From the latter point of view, fibre optics catalytic probes (FOCP) have a definite advantage: as any connection is made optical, they are completely immune to stray effects caused by high frequency electromagnetic field /35-38/. On the other hand, the FOCPs cannot measure low densities of O atoms.

Figure 2 represents measured values of O density in inductively coupled RF plasma created in a discharge tube made from borosilicate glass. Measurements were performed with a FOCP. One can observe that the O density does not depend much on RF power as long as the pressure is low. As the pressure is increased, the O density increases monotonously until it reaches a broad maximum. At high pressure, the O density decreases with increasing power. The appearance of maxima on the curves presented in Figure 2 is explained by different mechanisms of oxygen atom production and loss. At low pressure the O density is limited by surface effects rather than the discharge power. At high pressure the limiting factor is the poor density of electrons as well as their temperature. At even high-

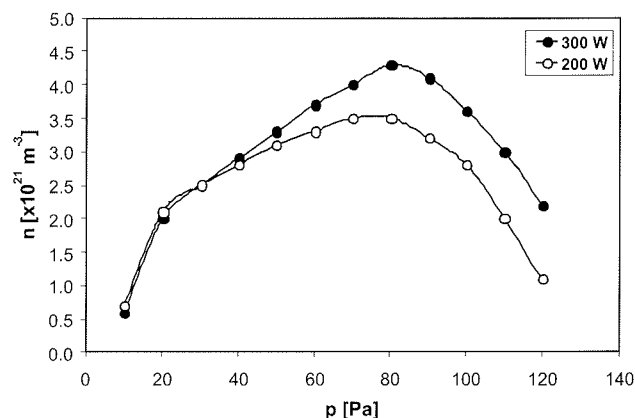


Fig. 2. Density of neutral oxygen atoms in a glass discharge tube with the inner diameter of 3.6mm versus pressure. The parameter is the discharge power.

er pressure the gas-phase atom loss by three-body would become important if the power were further increased. The optimal conditions for a large O density are met at pressure between about 50 and 100 Pa. In this range, the O density depends largely on the discharge power: a higher power causes a higher density. The pressure at which the maximum appears depends on power: at higher power the maximum is shifted to a higher pressure. In any case, the theoretical limit of the O density is full dissociation.

4 Interaction of plasma radicals with sample surfaces

The interaction of inductively coupled oxygen plasma with solid materials is almost entirely potential. As shown in upper text, the ion density is usually below 10^{16} m^{-3} and their kinetic energy at the sample surface about 10 eV. On the other hand we have neutral atoms with the density often exceeding 10^{21} m^{-3} . The dissociation degree therefore exceeds the ionization fraction by 5 orders of magnitude. A large flux of O atoms onto a sample surface assures rich surface chemistry if the samples are organic materials. The first effect of interaction is surface function-

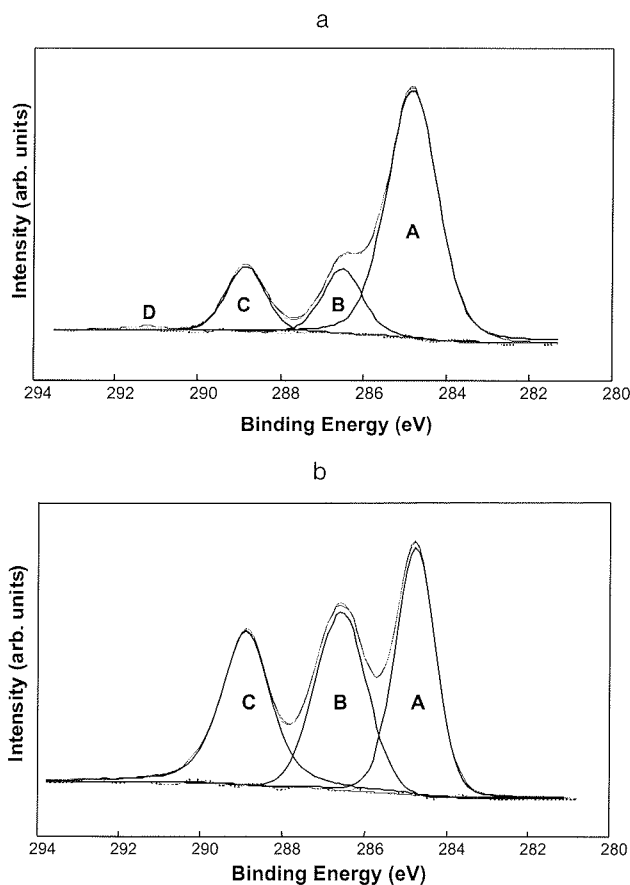


Fig. 3. High resolution XPS C1s peak of polyethyleneterephthalate. a) before and b) after plasma treatment for 1s. The O atom density is $6 \times 10^{21} \text{ m}^{-3}$. The peak A corresponds to C-C bond, B corresponds to C-O bond, C corresponds to O=C-C bond. D is the $\pi^*-\pi$ sh up.

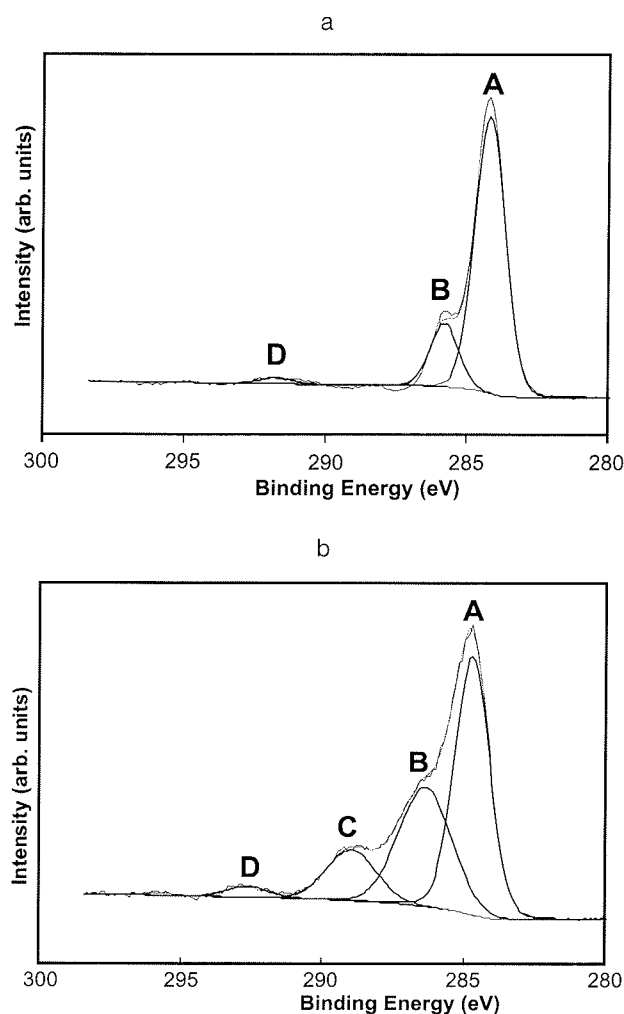


Fig. 4. High resolution XPS C1s peak of polyethersulphone. a) before and b) after plasma treatment for 1s. The O atom density is $6 \times 10^{21} \text{ m}^{-3}$.

alization with oxygen-rich functional groups. Next effect is slow etching of the organic material. Since the interaction is almost purely potential, the etching largely depends on the nature and structure of organic materials.

The appearance of the O-rich functional groups is best monitored by X-ray Photoelectron Spectroscopy (XPS) / 43-45/. The resulting surface activation (change of surface energy) is often measured by a contact angle of a water drop, while the distribution of different particles (fillings) in a polymer matrix composite is best monitored by a Scanning Electron Microscopy / 46-50/. The appearance of the reaction products is often detected by Optical Emission Spectroscopy (OES) [51/].

4.1 Surface activation

The first effect of oxygen plasma treatment of organic materials is surface activation. Figure 3 represents the effect of oxygen plasma treatment of polyethyleneterephthalate. Figure 3a is the carbon C1s peak obtained by a high-resolution XPS. The carbon is almost entirely bonded to other

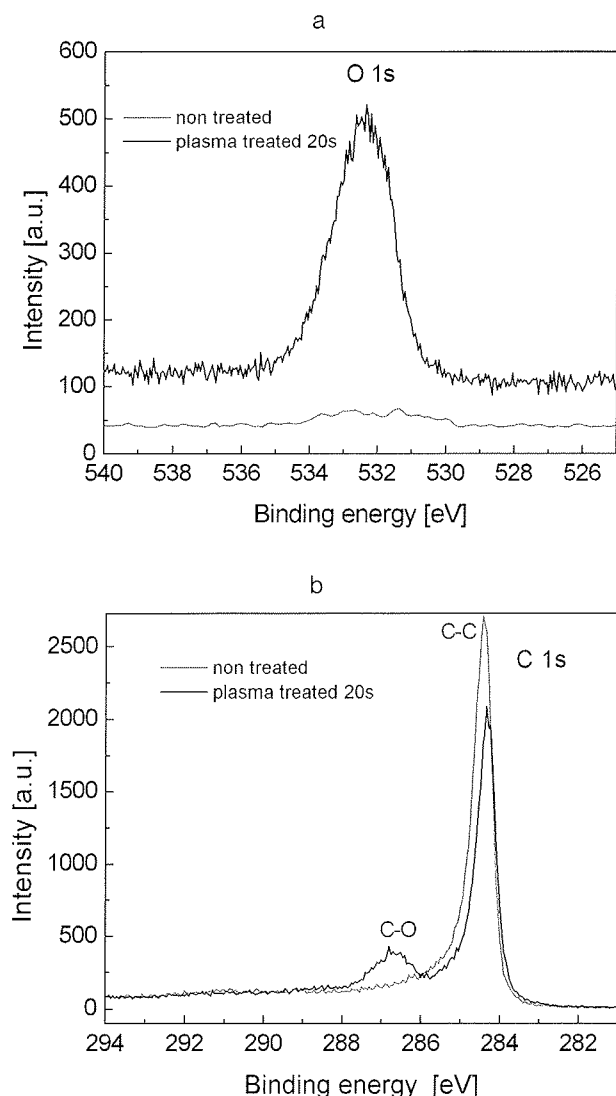


Fig. 5. High resolution XPS analysis of electrolytic graphite. a) O1s peak before and after plasma treatment for 20s, b) C1s peak before and after plasma treatment for 20s.

carbon atoms and some oxygen is presented in the form of ester group. The sample is exposed to inductively coupled oxygen plasma for 1 second. The carbon peak after this short plasma treatment is shown in Figure 3b. The peak is now enriched with oxygen functional groups. The surface of this material is saturated with functional groups in a second – further treatment does not influence the concentration of the groups on the surface.

Next example of quick plasma activation is presented in Figure 4. In this case, the organic material to be activated is polyethersulphone – a polymer containing sulphur. The C1s peak before plasma treatment is presented in Figure 4a, while after the treatment it is shown in Figure 4b. As in the case of polyethyleneterephthalate, the treatment time is only 1 second. The surface is quickly saturated with oxygen rich functional groups such as C-O (peak B in the spectrum) and C=O (peak C). The most energetic peak (D) is a satellite peak ($\pi \rightarrow \pi^*$).

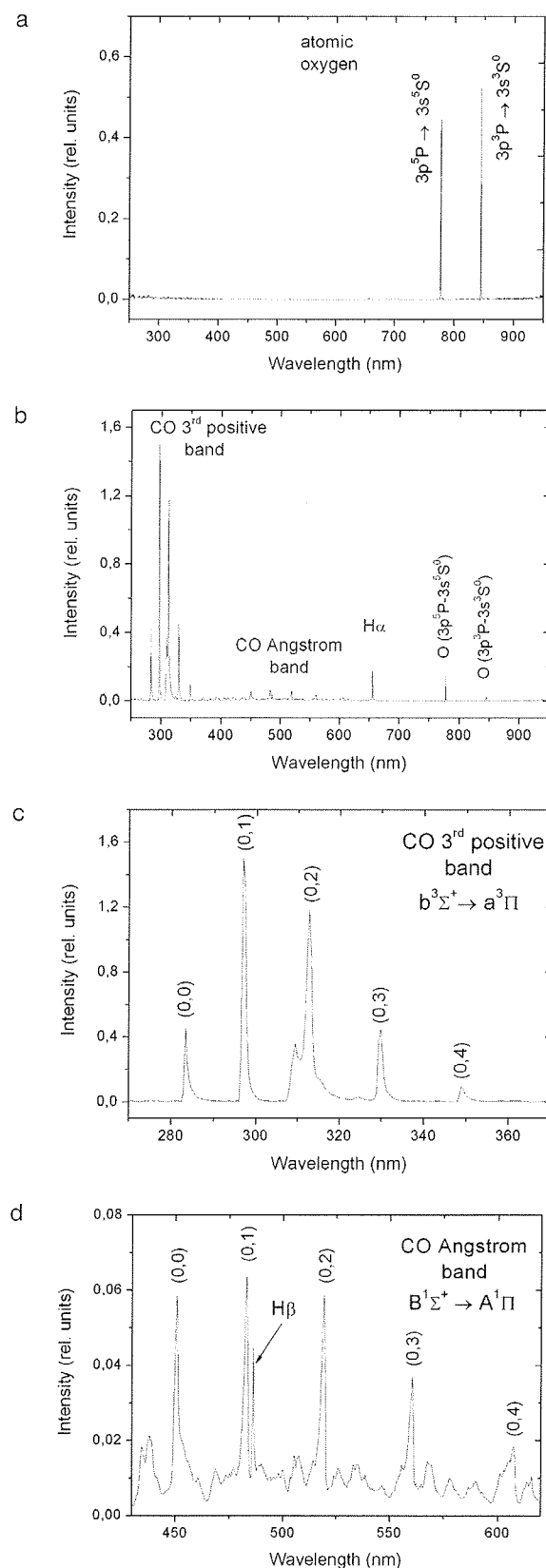


Fig. 6 Optical emission spectroscopy of oxygen plasma. a) before etching of organic material, b) during extensive etching, c) detail spectrum of the CO band corresponding to transitions within the 3rd positive system, d) detailed spectrum of the Angstrom band.

Apart from organic materials, other forms of carbon are also activated by oxygen plasma treatment, but the required treatment time may be longer. Figure 5 demonstrates activation of pure electrolytic graphite. In this case, the required treatment time is about 20 s. Figure 5a represents the high resolution XPS O1s peak before and after the plasma treatment, while Figure 5b represents the C1s peak. As expected, there is no oxygen bonded to untreated graphite, but the 20 s treatment cause an appearance of oxygen bonded in the form of C – O bond.

4.2 Polymer etching

As the surface is saturated with chemically bonded oxygen, the next step is slow chemical etching of carbon material. The etching rate depends on the type of material, its temperature, and the flux of oxygen atoms on the surface of the sample. The evidence of etching can be obtained by Optical Emission Spectroscopy. A simple optical spectrometer is good enough to monitor the appearance of the oxidation products. Figure 6a is a typical OES spectrum

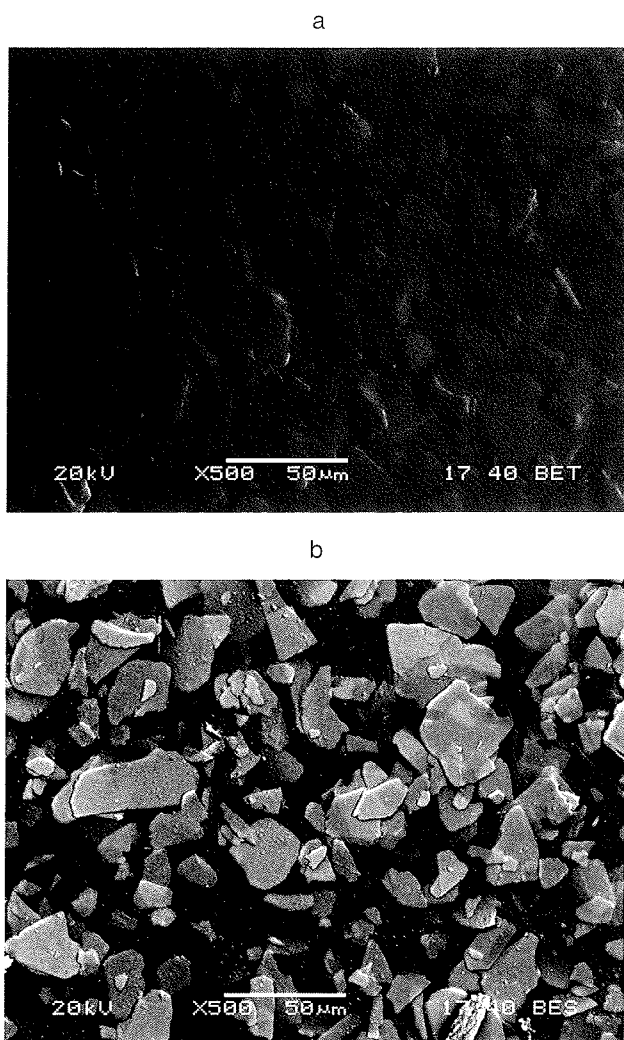


Fig. 7. SEM image of a metal paint with a pearl effect. a) untreated sample, b) sample treated in oxygen plasma for 40s. The O atom density is $8 \times 10^{21} \text{ m}^{-3}$.

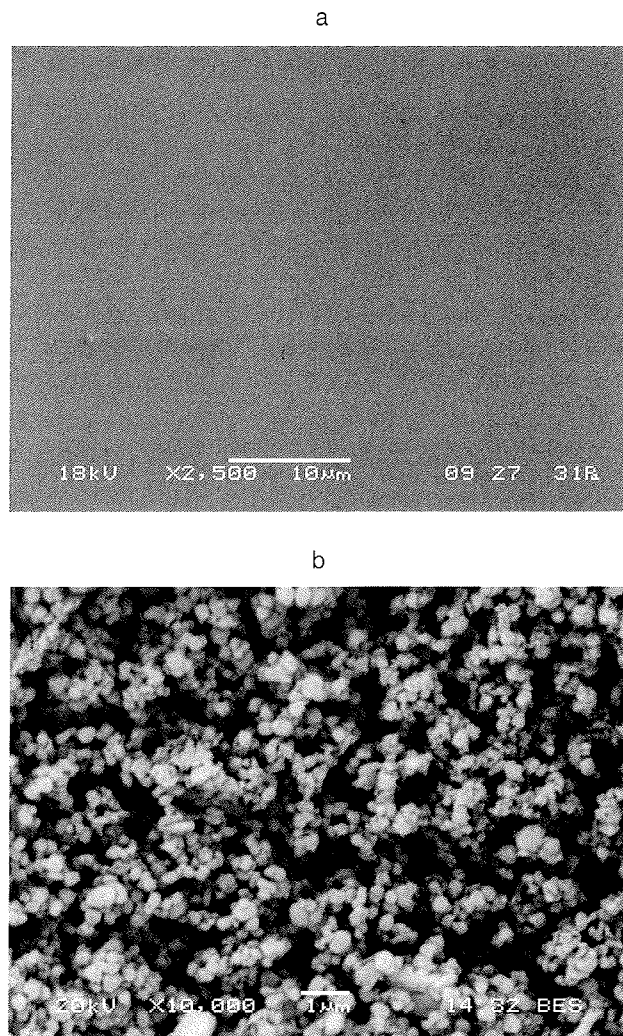


Fig. 8. SEM image of a powder coating. a) untreated sample, b) sample treated in oxygen plasma for 300s. The O atom density is $6 \times 10^{20} \text{ m}^{-3}$.

from oxygen plasma before etching of organic materials. The only features worth mentioning are the oxygen atoms peaks at 777 nm and 845 nm. Other peaks are so small that cannot be visible in Figure 6a. As etching of organic materials starts, the OES spectrum becomes richer as shown in Figure 6b. The peaks that correspond to CO bands appear. Figure 6c is a detail of the CO band corresponding to the transition in the 3rd positive system, while Figure 6d represents the emission due to CO transitions in the Angstrom band. Optical emission spectroscopy therefore represents a powerful tool for detection etching of carbon-containing compounds. Since CO is normally not presented in oxygen plasma in reasonable concentration, the appearance of the CO bands indicate etching of carbon containing materials.

4.3 Selective etching of composites

Composite materials with a polymer matrix are nowadays widely used as bulk materials and films. They combine the properties of polymers (easy installation, low price) and the

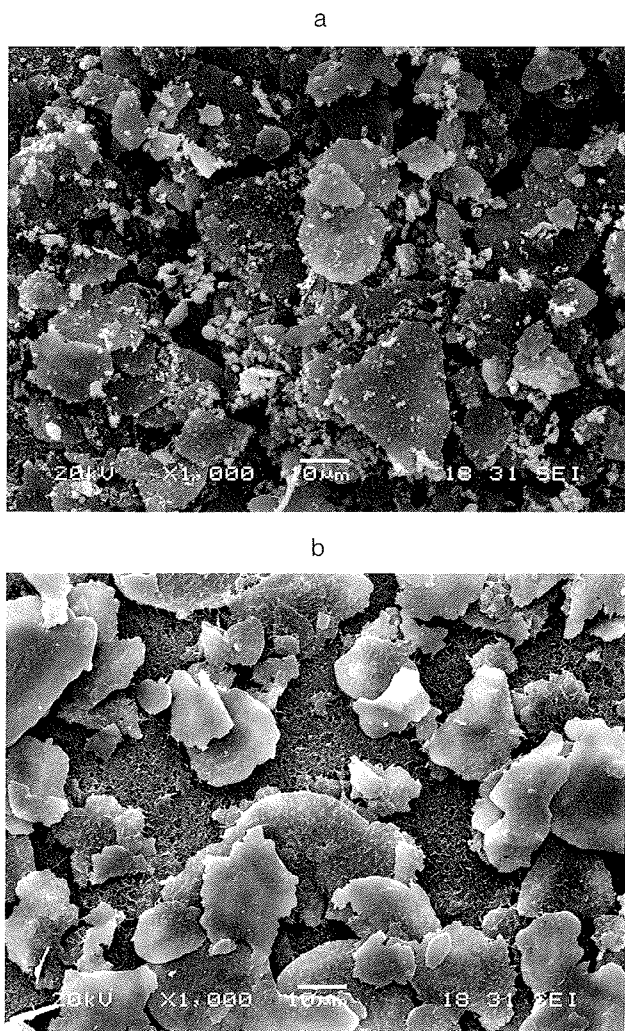


Fig. 9. SEM image of similar samples produced by two different producers. The plasma parameters were as follows: treatment time 120s, O atom density $2 \times 10^{21} \text{ m}^{-3}$.

fillers (good mechanical, electrical and optical properties). Many materials referred as plastics are actually composites. The most usual fillers are pigments – they are used to give the material its colour. Different fibres are used to increase the material strength and toughness. Graphite is

often used to increase electrical conductivity, while different coatings and paints are actually composites with a variety of fillers. A typical paint for metal, for instance is a composite of at least 5 different fillers distributed in the polymer matrix. The characteristics of the composites depend on the type of polymer, the type and concentration of the fillers, and the production procedure. They often depend also on distribution and in some cases even orientation of the fillers in the polymer matrix. The term “pigment dispersion” in paint coatings describes the relative amount of pigment aggregates and agglomerates in solid media. It affects gloss and haze of the final coating and may also change viscosity of the coating. Dispersion of pigments is influenced by the properties of coating components and by the production process.

It is difficult to detect the exact distribution of fillers in the polymer matrix. Namely, the uppermost material is polymer that hides the fillers. The best way of making fillers visible is a gentle removal of the polymer. The treatment should leave the fillers intact and should be performed at low temperature to avoid any deformation of the polymer matrix. The best way of doing so is to perform low temperature etching by inductively coupled oxygen plasma. As mentioned before, the interaction of such oxygen plasma with the solid material is almost entirely potential: oxygen atoms react with polymer matrix while leaving the fillers fairly intact. The first example of such treatment is a coating with mica flakes. Figure 7a is the SEM image of the untreated sample, while Figure 7b represents the image of the same sample exposed to oxygen plasma for 30 s. Comparison of Figures 7a and 7b clearly shows a high etching selectivity obtained by inductively coupled oxygen plasma: the polymer is effectively etched, while the mica flakes are left intact.

Mild oxygen plasma treatment is even selective enough to have different etching rates for two different organic materials. Figure 8 represents results of the etching of paint for metal. Figure 8a is the SEM image of untreated sample, while Figure 8b represents the same paint after plasma treatment. While the original surface is perfectly flat (covered by the polymer), the surface of plasma treated sample is covered with small perfectly spherical features. These spheres are actually organic pigments. The structure of

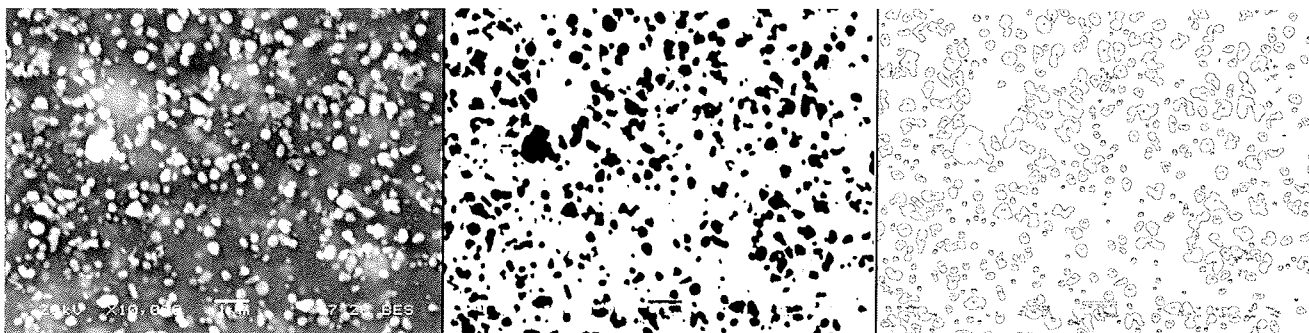


Fig. 10. SEM image of a sample before and after the image modification and outlined particles detected with appropriate program.

the organic pigments is different from the polymer matrix. The oxygen plasma is obviously gentle enough to distinguish between the polymer and the organic pigment. While polymer is etched at a high rate, the pigments are practically not etched at all, as observed by comparison of Figure 8 a and b.

The oxygen plasma treatment is used for study of fillers type, size and distribution in composites in order to detect small variations of similar products produced by different procedures. Figure 9 represents SEM images of similar products by two different producers. The similarity of the products is so high that classical testing of the two materials does not show any appreciable difference between them. The oxygen plasma etching, however, reveals small but important differences between the products in Figure 9 a and b. The product presented in Figure 9a is rich in small particles with the dimension of about 1 μ m, while these particles are absent in the product shown in Figure 9b. Plasma etching of such products actually enables the reverse engineering. If the type and concentration of fillers in a product are unknown, one can learn about them by etching the material with oxygen plasma and image the surface by a SEM.

Advanced software allows for quantification of the filler distribution in the polymer matrix composites. Figure 10 shows the appropriated steps done to study the size distribution of filler grains. The left figure is the SEM image of the plasma etched material. The middle figure is the negative contrast black/white micrograph. The right figure 3 shows the results of particle detection using the appropriate software program. The results of the image analysis of these three micrographs are presented in the Figure 11, where the size distribution of pigment particles is shown. Large particles, of diameter greater than 2 μ m, were excluded from the calculation because of their small population in the micrographs. The results in Figure 11 are shown for three mate-

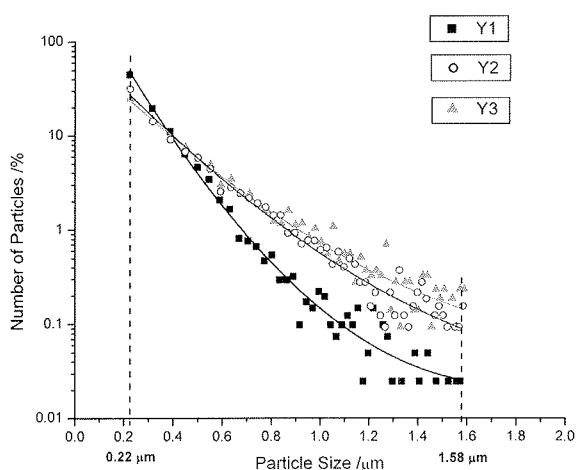


Fig. 11. Particle diameter distribution in samples produced by three different procedures marked as Y1, Y2 and Y3.

rials with same ingredients but different production procedure.

5 Conclusions

Highly reactive oxygen plasma is obtained in inductively coupled RF discharges. The degree of ionization is often of the order of 10^{-6} while the dissociation fraction easily exceeds 10%. The neutral gas temperature is kept close to room temperature since there is practically no mechanism heating the neutral gas. The high dissociation rate, low kinetic temperature, low ion density and low plasma potential allow for practically pure potential interaction of plasma radicals with solid materials exposed to plasma. The etching of samples is extremely selective: while organic materials are etched, the inorganic materials are not etched at all. The etching rate depends on the type of organic materials. Simple polymers are etched at relatively high rate while graphite is practically not etched at all. Even different types of organic materials are etched at different rates. While epoxy resin is etched at a relatively high rate, the organic pigments are virtually untouched. This extremely high etching selectivity allows for development a method for determination of the distribution and orientation of fillers in polymer matrix composites. Several examples of the practical application of this technology are presented. The choice of plasma parameters depend on characteristics of particular samples. High etching rate is obtained using plasma with a high atom density, but extremely high etching selectivity is obtained using plasma with a moderate O density.

References

- /1/ M. R. Wertheimer, L. Martinu, E. M. Liston, Plasma sources for polymer surface treatment, Handbook of thin film Process Technology, ed. by D.A. Glocker and S.I. Shah. Bristol, Inst. of Physics Publishing, Bristol, 1998.
- /2/ K. G. Pruden, G. B. Raupp, S. P. Beaudoin, J. Vac. Sci. Technol. B, vol. 21, pp. 1496, 2003.
- /3/ J. S. Kim, F. Cacialli, R. Friend, Thin Solid Films, vol. 445, pp. 358, 2003.
- /4/ S. Gomez, P. G. Steen, W. G. Graham, Appl. Phys. Lett., vol. 81, pp. 19, 2002.
- /5/ H. Singh, J. W. Coburn, D. B. Graves, J. Appl. Phys., vol. 88, pp. 3748, 2000.
- /6/ D. J. Wilson, N. P. Rhodes, R. L. Williams, Biomaterials, vol. 24, pp. 5069, 2003.
- /7/ Z. Y. Wu, N. Xanthopoulos, F. Reymond, J. S. Rossier, H. H. Girault, Electrophoresis, vol. 23, pp. 782, 2002.
- /8/ M. Mozetic, A. Zalar, Mater. Sci. Forum, vol. 437, pp. 81, 2003.
- /9/ A. G. Whittaker, E. M. Graham, R. L. Baxter, A. C. Jones, P. R. Richardson, G. Meek, G. A. Campbell, A. Aitken, H. C. Baxter, J. Hosp. Infect., vol. 56, pp. 37, 2004.
- /10/ K. Gorna, S. Gogolewski, Polym. Degrad. Stabil., vol. 79, pp. 475, 2003.
- /11/ M. Nagatsu, F. Terashita, Y. Koide, Jap. J. Appl. Phys, vol. 42, pp. L856, 2003.
- /12/ M. K. Gunde, M. Kunaver, Appl. Spect., vol. 57, pp. 1266, 2003.

- /13/ M. Kunaver, M. K. Gunde, M. Mozetic, M. Kunaver, A. Hrovat, Surf. Coat. Int. B, vol. 86, pp. 175, 2003.
- /14/ M. Mozetic, U. Cvelbar, M. K. Sunkara, S. Vaddiraju, Adv. Mater., vol. 17, pp. 2138, 2005.
- /15/ A. Vesel, M. Mozetic, A. Drenik, S. Milosevic, N. Krstulovic, M. Balat-Pichelin, I. Poberaj, D. Babic, Plasma Chem. Plasma Proc., vol. 26, pp. 577, 2006.
- /16/ A. Vesel, M. Mozetic, A. Zalar, Appl. Surf. Sci., vol. 200, pp. 94, 2002.
- /17/ M. Mozetic, Vacuum, vol. 71, pp. 237, 2003.
- /18/ U. Cvelbar, D. Vujosevic, Z. Vratnica, M. Mozetic, J. Phys. D Appl. Phys., vol. 39, pp. 3487, 2006.
- /19/ A. Ricard, Reactive plasmas, SFV, 1996.
- /20/ A. Ricard, V. Monna, Plasma Sourc. Sci. Technol., vol. 11, pp. A150, 2002.
- /21/ A. Vesel, M. Mozetic, Vacuum, vol. 61, pp. 373, 2001.
- /22/ S. Villeger, S. Cousty, A. Ricard, M. Sixou, J. Phys. D Appl. Phys., vol. 36, pp. L60, 2003.
- /23/ A. Drenik, U. Cvelbar, A. Vesel, M. Mozetic, Inf. MIDEM, vol. 35, pp. 85, 2005.
- /24/ J. J. Robbins, R. T. Alexander, W. Xiao, T. L. Vincent, C. A. Wolden, Thin Solid Films, vol. 406, pp. 145, 2002.
- /25/ M. C. Kim, S. H. Yang, J. H. Boo, J. G. Han, Surf. Coat. Technol., vol. 174, pp. 839, 2003.
- /26/ A. Granier, M. Vervloet, K. Aumaille, C. Vallee, Plasma Sourc. Sci. Technol., vol. 12, pp. 89, 2003.
- /27/ H. Biederman, V. Stelmashuk, I. Kholodkov, A. Choukourov, D. Slavinska, Surf. Coat. Technol., vol. 174, pp. 27, 2003.
- /28/ G. F. Leu, A. Brockhaus, J. Engemann, Surf. Coat. Technol., vol. 174, pp. 928, 2003.
- /29/ Y. C. Hong, H. S. Uhm, Phys. Plasmas, vol. 10, pp. 3410, 2003.
- /30/ G. B. I. Scott, D. A. Fairley, D. B. Milligan, C. G. Freeman, M. J. McEwan, J. Phys. Chem. A, vol. 103, pp. 7470, 1999.
- /31/ L. Elias, E. A. Ogrizlo, H. I. Schiff, Can. J. Chem., vol. 37, pp. 1680, 1959.
- /32/ M. R. Carruth, R. F. DeHaye, J. K. Norwood, A. F. Whitaker, Rev. Sci. Instr., vol. 61, pp. 1211, 1990.
- /33/ I. Sorli, R. J. Rocak, Vac. Sci. Technol. A, vol. 18, pp. 338, 2000.
- /34/ M. Mozetic, A. Vesel, M. Gaillard, A. Ricard, Plasmas Polym., vol. 6, pp. 41, 2001.
- /35/ D. Babič, I. Poberaj, M. Mozetič, Rev. Sci. Instr., vol. 72, pp. 4110, 2001.
- /36/ I. Poberaj, D. Babič, M. Mozetič, J. Vac. Sci. Technol. A, vol. 20, pp. 189, 2002.
- /37/ M. Mozetic, A. Ricard, D. Babic, I. Poberaj, J. Levaton, V. Monna, U. Cvelbar, J. Vac. Sci. Technol. A, vol. 21, pp. 369, 2003.
- /38/ M. Balat-Pichelin, A. Vesel, Chem. Phys., vol. 327, pp. 112, 2006.
- /39/ A. Vesel, M. Mozetic, M. Balat-Pichelin, Vacuum, in press, (doi:10.1016/j.vacuum.2007.02.003), 2007.
- /40/ M. Mozetic, A. Vesel, U. Cvelbar, A. Ricard, Plasma Chem. Plasma Process., vol. 26, pp. 103, 2006.
- /41/ M. Mozetic, A. Vesel, V. Monna, A. Ricard, Vacuum, vol. 71, pp. 201, 2003.
- /42/ M. Mozetic, U. Cvelbar, A. Vesel, A. Ricard, D. Babic, I. Poberaj, J. Appl. Phys., vol. 97, pp. 103308-1, 2005.
- /43/ T. Vrlinic, A. Vesel, U. Cvelbar, M. Krajnc, M. Mozetic, Surf. Interface Anal., in press, (DOI: 10.1002/sia.2548), 2007.
- /44/ A. Vesel, M. Mozetic, A. Zalar, Vacuum, in press, 2007.
- /45/ A. Vesel, M. Mozetic, J. Kovac, A. Zalar, Appl. Surf. Sci., vol. 253, pp. 2941, 2006.
- /46/ M. Mozetic, A. Zalar, P. Panjan, M. Bele, S. Pejovnik, R. Grmek, Thin solid films, vol. 376, pp. 5, 2000.
- /47/ M. K. Gunde, M. Kunaver, M. Mozetic, P. Pelicon, J. Simcic, M. Budnar, M. Bele, Surf. Coat. Int., Part B, Coat. Trans., vol. 85, pp. 115, 2002.
- /48/ M. Kunaver, M. K. Gunde, M. Mozetic, A. Hrovat, Dyes Pigm., vol. 57, pp. 235, 2003.
- /49/ M. K. Gunde, M. Kunaver, M. Mozetic, A. Hrovat, Powder Technol., vol. 148, pp. 64, 2004.
- /50/ M. Kunaver, M. Mozetic, M. K. Gunde, Thin solid films, vol. 459, pp. 115, 2004.
- /51/ N. Krstulovic, I. Labazan, S. Milosevic, U. Cvelbar, A. Vesel, M. Mozetic, J. Phys. D Appl. Phys., vol. 39, pp. 3799, 2006.

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