Study of Optical Properties and Molecular Structure of Plasma Polymerized Diethylene Glycol Dimethyl Ether

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Ethylene glycol ethers have been used as monomers in plasma polymerization process to produce different types of coatings in modern industry. Due to their high adhesion characteristic they can be used as coating on several different types of materials. The films have essentially the same properties of conventional polymers and also good resistance to the action of acids and bases as occurs in conventional polymers chemically produced with this family of monomers. In this work we used a stainless steel plasma reactor to produce thin polymeric films from low pressure RF excited plasma of diethylene glycol dimethyl ether. Plasmas were produced at 150 mTorr in the range of 10 W to 40 W. Films were growth on silicon and quartz substrates. The molecular structure of plasma polymerized films and their optical properties were analyzed by Fourier Transform Infrared Spectroscopy (FTIR) and Ultraviolet-Visible Spectroscopy. The IR spectra show C-H stretching at 3000-2900 cm^{-1}, C=O stretching at 1730-1650 cm^{-1}, C-H bending at 1440-1380 cm^{-1}, C-O and C-O-C stretching at 1200-1000 cm^{-1}. The concentrations of C-H, C-O and C-O-C were investigated for different values of RF power coupled to the plasma reactor. It can be seen that the C-H concentration increases from 0.55 to 1.0 au (arbitrary unit) with the increase of RF power from 10 to 40 W The concentration of C-O and C-O-C decreases from 1.0 to 0.5 au in the same range of RF power. The refraction index increased from 1.48 to 1.56 with the increase of RF power from 10 to 40 W. The optical gap calculated from absorption coefficient decreased from 4.6 to 3.35 eV with the increase of RF from 10 to 40 W. Due to its optical and hydrophilic characteristics these films may be used, for instance, in ophthalmic industries as glasses lenses coatings.

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Superhard Vacuum – Arc TiN Coatings

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Vacuum-arc TiN coatings of hardness ranging between 40 and 68 GPa, and with the H/E^* ratio amounting up to 0.149, were obtained by the method of plasma-based ion implantation and deposition. In the process, the substrate temperature was ranging from 105 to 465°C. After holding the coated samples for 3 months at room temperature, or on vacuum annealing of the samples for 2 hours at a temperature of 700°C, the coating hardness decreased by 15 to 30%. The paper describes the mode of deposition and the results of investigations of the coatings.

Plasma Treatment of Powder Materials

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Plasma modification of powder has recently attracted much interest because of new prospects to control the interfacial properties. Low-pressure plasma modification in fluidized bed has been most frequently applied, but application of mechanical stirring appears very promising for industrial-scale application. It is shown that this penetration substantially reduces the process time. The PE parts sintered from the plasma-modified powder are characterized with high surface tension, which allows e.g. direct painting or adhesive bonding without any additional pretreatment. The plasma modification also significantly enhances the adhesion of the polymer powder to the substrate.

Comparison of model calculations and experimental investigation indicated the role of the penetration of the active species under the upper layer of the powder modifying also the powder placed in deeper layers. It is shown that this penetration substantially reduces the process time. Both air and oxygen plasma treatments show an increase of the capillarity of the treated powder. The plasma modification also significantly enhances the adhesion of the polymer to the substrate.

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Plasma Drift in Dual Magnetron Discharge

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Dual magnetron (DM) is an advanced sputtering system which is effectively used in the deposition of thin films, particularly oxides and multiphase coatings. Main advantage of this system lies in a removal of the arcing on the surface of the magnetron target and the problem of disappearing anode in single magnetron system during reactive sputtering of electrically insulating oxides. In principal, DM is composed of two magnetrons and can be realized in two main configurations – either in mirror magnetic field configuration or in closed magnetic field configuration. For the former case, a repulsive **B** field formed between the targets of magnetrons results in generation of two separated plasma discharges. On the other hand, in the case of closed magnetic field configuration, an attractive **B** field between magnetrons results in the generation of one single discharge confined between targets of both magnetrons.

The DM, however, strongly differs also in the distribution of magnetic field lines **B** depending on an angle α between axes of both magnetrons. For the DM system with magnetrons tilted at certain angle α, a gradient of magnetic field **B** (∇**B**), perpendicular to the

lines of **B** is formed. The $\nabla\mathbf{B}$ together with the vector **B** generates a drift of the plasma from the xy-plane along the z-axis. Assuming that a cyclotron rotation of charged particles takes place in the plane perpendicular to the magnetic field lines **B**, plasma drifts in the plane perpendicular to the magnetic field lines **B**. This drift is called the gradient drift and its velocity along the z-axis can be determined by the following formula:

$$\boldsymbol{v}_d = -\frac{W_\perp}{qB_x^2}\nabla_\perp B_x \times \hat{x}$$

Here $\boldsymbol{v_d}$ is the vector of drift velocity, $W_\perp$ is the kinetic energy of particle perpendicular to the field line, q is the electric charge of particle, B_x is the component of magnetic induction **B** and $\hat{x}$ is the unit vector in the direction of magnetic field line. This equation clearly shows that plasma should drifts perpendicularly to the xy-plane. This drift of the plasma discharge along z-axis was really observed experimentally in the tilted DM systems for both magnetic configurations (mirror magnetic field and closed magnetic field). However, no drift of the discharge exists in the DM with face-to-face magnetron configuration ($\alpha = 180°$) due to an axially symmetrical distribution of the magnetic field lines. All of these observations were done in the DM sputtering system under following conditions: I = 0.5 A, f_r = 100 kHz and p = 0.5 Pa. Magnetrons were equipped with Ti targets of 50 mm in diameter and magnitude of the magnetic field at their surface was approximately 200 mT.

Simultaneously with experiments, a computer modeling was employed to describe above mentioned plasma drift phenomenon under various geometric and magnetic configurations of DM system and results obtained are presented.

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Comparison of Low- Pressure Plasma with Atmospheric-Pressure Plasma Treatment of Aluminum Surfaces

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In recent years, there is a large interest in surface modification of aluminium because of their wide application in industry. Many machine parts, mainly used in the automotive, aerospace and also architectural branch are made of aluminium. Sheet metals are generally coated by oils layer for temporally corrosion protection or by lubricants for friction reduction during metal-forming processes. Traditional methods of surface cleaning are mostly liquid and chemical processes, using organic solvents and aggressive chemicals. However, the ecological requirements force the industry to search for alternative environmentally friendly methods. Over the two past decades, plasma surface treatment techniques have been extensively investigated, since they are not as harmful for the environment as the

conventional ones. The advantages of the plasma treatment have been well known in the laboratories for a long time.

This paper will present the investigations of alumina surface treatment by two types of plasma sources: a novel atmospheric-pressure ambient air plasma device based on the use of Diffuse Coplanar Surface Barrier Discharge (DCSBD) and capacitive coupled low-pressure RF discharge plasma source operating at 400 kHz frequency. The aims of our study are to compare possibility of using plasma generated by DCSBD and by RF low-pressure discharge to modification of aluminium surface. We provided measurements of contact angle after plasma treatment with respect to treatment time and measurements of ageing effect. The plasma treated samples were analyzed by AFM. The plasma conditions were characterised by electric measurements of the discharges. The results bring a better understanding of surface treatment processes using non-isothermal atmospheric-pressure plasma and its advantages for surface treatment.

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The Observing of Surface Changes of PET and POP after Plasma Treatment

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Surface textiles made of PET and POP fibres have wide industrial applications. These materials are mostly hydrophobic. That's the reason to change hydrophobic features to water-receptive.

One of the most important technologies of surface modifications is based on modification realized by plasma. In this experiment, the low energy plasma was used.

Surface properties of synthetic fibres and sheets made of POP and PES materials, treated by plasma (DCSBD) have been studied by XPS (X-Ray Photoelectron Spectroscopy), FTIR spectroscopy (Fourier Transform Infrared Spectroscopy), AFM (Atomic Force Microscope) and SEM (Scanning Electron Microscopy). Properties of chemical changes were tested by FTIR, changes of surface were tested by SEM.

The XPS technique is highly surface specific due to the short range of the photoelectrons that are excited from the solid. The energy of the photoelectrons leaving the sample is determined using a CHA and this gives a spectrum with a series of photoelectron peaks. The binding energy of the peaks is characteristic of each element.

Measurement was done by use of FTIR (PERKIN-ELMER). Primary objective of experiment was to describe changes of chemical bonds and formation of new chemical groups after the treatment.

Atomic Force Microscopy is the method used for characterization of prepared sub-micron optical elements.

The photographs of POP and PES fabrics were made by use of scanning electron microscope VEGA. Detection of structure breaks and structural changes of fibre surfaces, made by plasma, was the objective.

The surface hydrophility of POP and PES polymers was increased. It is possible to predict this method as new environmental method of hydrophilic treatment of synthetic fibres.

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The Double M-effect Induced by Noble Gases Activated with Negative Ions

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The M-effect (monochromatization–effect) is a powerful tool which can give high intensity monochromatic one line spectra with a certain wavelength depending on the type of used gas mixtures to generate plasma state. The effect consists in the emission of a single spectral line of plasmas ignited in certain gas mixtures. The main condition to obtain the M effect is the presence of an electropositive and an electronegative (for example: Hydrogen) gas mixture. A monochrome radiation was obtained in each of these gas mixtures (e.g. Hydrogen and Neon or Hydrogen and Argon) the wavelengths of the emitted lines being 585.3 nm for the emission spectrum of Ne and 750.4 nm for Ar in the case of Ne+ H_2 or Ar+H_2. Both recorded spectra were each unique and monochrome.

In this paper we prove the general character of this effect, i.e. if the optical emission spectra reduced to nearly one line can be observed also in other gas mixture discharges, for example in the case of one electronegative gas and two electropositive gases.

This discharge with three elements Ne and Ar with H_2 have proved the existence of the double M-effect. The results suggest that the simultaneous M-effect is independent of total gas pressure as long as the relative concentration of the three gases remains unchanged. An interesting feature of the relative intensities has been observed at different percentages of hydrogen added in the partial pressure of the mixture. Different other mixtures, as Xe + Ne + H_2 and Ar + Xe +H_2 have been studied. In all these cases, the M-effect appeared without doubt.

The mechanism responsible for the generation of the monochrome radiation is based on the elementary process of three body collision together with the resonant radiation of plasma or of plasma due to trapped resonance radiation. We explained this with the diagram of energy levels of particles involved in the process. Additional processes including two particle interactions like resonant radiation trapping or metastable state are parts of M – effect. This increased performance extends the area of gas mixtures in which the M-effect can be established, especially ensure the generation of pulsed high voltages with frequencies up to 25 kV.

We proved the general character of the M-effect and we established the conditions to obtain M-effect. These results opened a new research area, with applications involving emission line sources including double M-effect. Further experiments to put in evidence the dependence of the double M-effect on other experimental parameters are under consideration.

* * *

Accelerated Nitridation and Oxidation by Plasma on Polyethylene

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Polyethylene (PE) is the most studied polymer probably because of its simple structure composed only by (-CH_2-) groups. The main applications of PE are related with its high hidrophobicity, low electric conductivity and low chemical activity in the field of environmental protection films, electric insulating materials and implant prosthetics. In particular, the medical uses have diversified continuously to include the replacement or modification of hips, articulations, bones, veins, eye tissues, etc. In some of those applications, the polymer has to work for long time in the middle of mechanical stress surrounded by reactive fluids, electrolytes and electric impulses. The most common chemical reactions usually involve oxidation and nitridation. Those conditions, individually or combined, gradually modify the initial characteristics of the polymer, reducing its efficiency.

In order to study accelerated oxidation and nitridation in PE, in this work, thin films of low density polyethylene were exposed to long continuous direct current glow discharge plasmas of oxygen and nitrogen. The physicochemical interaction depends on the the trajectory of the plasma particles, power, exposure time and geometric configuration. The PE substrates were treated in a vacuum camera with resistive electrode discharges, exposing the maximum area to the rain of charged particles. The power density applied to the polymers was 7.8 mW/mm^2 and the maximum energy, after 180 min, was 84 J/mm^2.

The results indicated that PE was oxidized and/or nitrided in approximately the same proportion, with atomic ratios between O/C=(0.07-0.15) and N/C=(0-0.17). The maximum values mean approximately 7 C atoms per each N or O atoms in the chains. The constant impact of high-energy particles on the surface promoted selective erosion, which produced fibered and folded morphologies of nano and micro dimensions. The erosion on the surface can be related to the ordered structures in the polymer, which increased and decreased, between 33% and 57%, along the treatment with both plasma gases. The treatment increased the hydrophilic nature of polyethylene in the first 30 min of exposition to the plasma, in which the contact angle of water decreased, from 70% in untreated PE, to 45% and 35% in the polymers processed with nitrogen and oxygen plasmas, respectively. The evolution of PE in these reactive atmospheres can be used to resemble the life of PE where oxidation and/or nitridation prevail.

* * *

Energy Balance on a Substrate in a Pulsed DC Plasma Jet Sputtering System during TiO_x Thin Film Deposition

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The total energy flux density delivered to an electrically isolated substrate in an low pressure pulsed DC hollow cathode plasma jet sputtering system during TiO_2 thin films deposition has been quantified. The plasma source was operated in constant average current mode and in a

mixture of argon and oxygen or only in pure argon working gas. A titanium nozzle served as the hollow cathode. The oxygen gas was fed into the reactor chamber via a separate port located sideways. The total energy flux density measurements were made using a planar calorimeter probe. The time-resolved Langmuir probe placed 10 mm above the substrate was used for plasma parameters measurements. The film thickness measurement by using of Alpha-step device helped us with a estimate of sputtered particles flux density on the substrate. The main results from the calorimeter probe show clearly that with increasing pulsing frequency from 500 Hz to 50 kHz the total energy flux density on the electrically isolated substrate increases for lower duty cycles (10% to 50%) and decreases for duty cycle 90%. Furthermore, course of the total energy flux density on the substrate as a function of duty cycle demonstrates a minimum at duty cycle 60% for both operation in pure argon in argon and oxygen mixture. The measured plasma parameters i.e. plasma density, electron temperature, plasma and floating potential allowed us to determine the individual contributions from the charged particles to the total energy flux density on the substrate. A detailed study on elementary processes i.e. recombination of oxygen atom, adsorption of Ti or O atoms and formation of the TiO_2 thin film on the substrate revealed a substantial influence of these processes on the energy balance on the substrate. Measured cathode voltage and discharge current waveforms demonstrated transient phenomena during ON to OFF and vice versa transitions. The experimental results indicated that the previously introduced model of the individual contributions to the total energy flux density on the floating substrate could be applied to the plasma jet sputtering system. Then the substantial part of the total energy influx density on the substrate comprises the kinetic energy of high-energy ions and electrons produced during overshoots of the cathode voltage at certain pulsing frequencies and duty cycles. The bombardment of a substrate by ions such high kinetic energy may lead to production of thin films of better quality – coating are denser, smoother etc.

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Effect of the Gas Mixture Composition on High-Temperature Behavior of Magnetron Sputtered Si-B-C-N Coatings

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Our preliminary investigation of oxidation resistance and thermal stability of the Si-B-C-N coatings to 1300 ^{o}C has indicated a strong effect of the gas mixture composition on coating properties. From this reason, further tests were carried out to investigate the high-temperature behavior of these coatings up to 1700 ^{o}C. The Si-B-C-N coatings (typically 2-3 µm thick) were deposited on Si, SiC and Cu substrates by dc magnetron co-sputtering using a single B_4C-Si target in nitrogen-argon gas mixture. The effect of the gas mixture composition (50 or 75 % of Ar) on the high-temperature behavior of the Si-B-C-N coatings was investigated using a symmetrical high-resolution Setaram TAG 2400 thermogravimetric system and differential scanning calorimeter DSC Labsys 1600 in a synthetic air and in an

inert gas (He, Ar). The elemental composition of the coatings was determined by Rutherford back-scattering spectrometry (Si, B, C, N, O, Ar) and elastic recoil detection method (H). The structure of the coatings was measured by XRD. The gas mixture composition was found to be a very important process parameter having a great impact on the elemental composition (especially on the N/Si ratio) and consequently on final properties of the Si-B-C-N coatings, such as oxidation resistance and thermal stability of their structure and mechanical properties. The coatings sputtered at a 50 % Ar fraction in the gas mixture exhibited extremely high oxidation resistance up to 1500 ^{o}C and preservation of the amorphous state even up to 1700 ^{o}C in air. No mass or structural changes of the coatings were also detected by TG and DSC analyses up to 1600 ^{o}C in an inert gas.

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Surface Free Energy Evaluation of Untreated and Plasma Treated Polymers in the Practical Courses

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Students of plasma physics usually obtain wide theoretical overview on the phenomena in ionized gases and plasma based technologies as well as some practical experience and skills in plasma sources and plasma diagnostics. In the field of surface diagnostics the situation is more complicated mainly in the field of practical experience and skill acquisition. The most limiting factor of current practical courses is the access to the analytical techniques due to their high costs.

In this work the implementation of surface free energy evaluation in practical courses is presented. Surface free energy (SFE) evaluation is one of the most important surface analytical techniques because of this parameter carries information about interfacial interactions such as adhesion, wettability of the surface etc. SFE evaluation technique plays key role in the process of characterization of surfaces after plasma treatment or the plasma processing of polymers.

This technique is based on determination of tangent contact angle of sessile liquid drop on the solid surface. Using several models (Zismann theory, Owen-Wendt-Raeble-Kaeble theory or so called Acid-Base theory) SFE can be calculated.

The practical exercise on the surface free energy evaluation is already prepared. In the frame of this course students obtain necessary theoretical background on SFE and its role in the surface interactions. They also obtain valuable practical skills on the SFE evaluation.

In this course students gain the experience with instrumentation for SFE evaluation and the physical factors that influence the accuracy of measurement (the equilibrium relaxation time of solid-liquid system, liquid evaporation, surface roughness and temperature, image contrast and influence of light exposure).

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Surface Energy Evaluation of Unhydrogenated DLC Thin Film Deposited by Thermionic Vacuum Arc (TVA) Method

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Diamond like carbon (DLC) thin films have drawn strong attention recently of the scientists owing to their remarcable poperties of the coating surfaces such as wear resistance, electrical properties, hardness, roughness, smoothness, low friction coefficients, chemical inertness.

The variation of the contact angle measurements with ion energy is believed to be correlated to the topography of the films. The aim of this paper is to make the surface energy evaluation by contact angle measurements of DLC films deposited on different substrates: glass plate, single crystalline silicon, stainless steel and alumina foil.

The deposition of the DLC thin films was carried out by the Thermionic Vacuum Arc (TVA) method. This is an original method for deposition of high purity thin films with compact structure and extremely smooth, just convenient for nanostructure film preparation. We mention only some of the sounding advantages of TVA method: the growing thin film is bombarded just during deposition with the ions of the depositing material in high vacuum conditions and more important, the energy of bombarding ions can be controlled and even changed during deposition.

The contact angle measurement were performed by establishing the tangent angle of a liquid drop with a solid surface, defined by the mechanical equilibrum of the drop under the action of three interfacial tension solid-vapor, solid-liquid, and liquid – vapor, by meaning of the performed analysis software See System. The testing liquids were water and ethylen glicol and the surface energy evaluation system were made on the basis of Wu state equation and Owens – Wend models.

The contact angle measurements have shown reproducible results of high values for high values of ion energy, whereas values ranging from 89,9 to 78,38 degrees for water and 51,9 to 61,98 degree for ethylene glycol were obtained at low ion energies, which implies 27,74 to 36,41 mJ/m^2 values of surface energy.

As we have previously reported, a higher number of uniformly spread diamond crystallites at higher ion energies, but of a lower size (<10 nm) were observed in the DLC films obtained by TVA. At lower ion energies the diamond crystallites were over 100 nm but very scarce. Therefore, wetability had reproducible values for the samples with lots of small features on the surface and it had a high variation of values on samples were large features but in small numbers were observed.

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Application of Atmospheric Pressure Microwave Plasma Source for Production of Hydrogen via Methane Reforming

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This work is aimed at atmospheric pressure microwave plasma source (MPS) for production of hydrogen via methane reforming with N_2 swirl. In the proposed method a high-flow rate waveguide-based coaxial-type MPS operated at high gas flow rates was used.

The main parts of the experimental setup used in this investigation were a microwave magnetron generator (2.45 GHz, 6 kW), microwave plasma source (MPS), microwave supplying and measuring system, and gas supplying system. The microwave power (up to 6 kW) was supplied from the magnetron to the MPS via a rectangular waveguide (WR-430) having a reduced-height section. The plug efficiency of the used microwave magnetron generator was higher than 66 %.

In our previous version of MPS the methane plasma could not be sustained at the absorbed microwave power lower than about 3000 W. The modified MPS presented in this paper allows to sustain the methane plasma at absorbed microwave power of 1000 W. In the new MPS, the narrow external electrode was introduced with the inner diameter of 46 mm, so microwave at frequency of 2.45 GHz could not be guided along the external electrode. This causes lower losses of microwave energy, i.e., the higher microwave power is delivered to the unit volume of the plasma. In the new MPS, the processed methane (175 l/min) was introduced to the plasma by the inner electrode. The outer diameter of the inner electrode was 20 mm. This inner electrode together with the external (inner) electrode form a section of microwave coaxial line, which causes that maximum of the electric field in the place where plasma is formed. We observed that the inner electrode improved the stability of plasma generation, especially at a high methane flow rate. The MPS was used for hydrogen production via methane reforming for two inner diameters ϕ of the inner electrode, i.e., ϕ = 6 mm and ϕ = 12 mm.

The plasma generation was stabilized by forming an additional nitrogen swirl flow (50 l/ min) in the quartz cylinder. The swirl gas held the discharge in the centre of the cylinder and thus protected the cylinder wall from overheating. As the swirl the nitrogen was used instead of air to avoid production of harmful oxides.

Concentration of H_2 and CH_4 in the gas exiting the discharge tube was measured with the gas chromatograph (SRI 8610C) and FTIR spectrophotometer (Perkin Elmer 16 PC).

The results of this investigations show that the hydrogen mass yield rate and the corresponding energetic hydrogen mass yield in the presented methane reforming by the new high-flow rate waveguide-based coaxial-type MPS were up to 432 g[H_2]/h and 418 g [H_2]/kWh, respectively. These parameters are better than both our previous results and those other plasma methods of hydrogen production (electron beam, gliding arc, plasmatron).

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Absolute Vacuum UV Emission from the Effluent of an Atmospheric Pressure Plasma Jet (APPJ) with Ar/Xe and Ar/Kr Mixtures in Ambient Air

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Among other non-equilibrium plasmas operating at normal pressure, atmospheric plasma jets (APPJ) have been established specifically for the local treatment of 3-D surfaces, e.g. inner walls of wells, trenches or cavities. The treatment of temperature-sensitive surfaces is of interest, in particular the interaction of the plasma with biological material, e.g. for cultivation, deactivation or remedial treatment of diseases.

It has been demonstrated that APPJ in Ar exhibit intense UV and VUV emissions. Radiation within this wavelength range along with chemical reactivity caused by free radicals plays an essential role for the applications listed above.

Here, the vacuum ultraviolet (VUV) emissions from an APPJ excited by radio frequency at 1.2 MHz in pure Ar and mixtures of Ar and Xe or Kr were analysed. The absolute radiance for these mixtures is measured in order to characterize the device for application, to tailor the emission spectrum and to illuminate the discharge mechanisms.

The jet produces a cone-like plasma (effluent) outside the nozzle (with a maximum plasma radius $r \approx 0.8$ mm and a length $L = 6$ mm) expanding into open air.

The optical emission was measured end on at different distances between the nozzle of the jet and the MgF_2 window, which seals the vacuum chamber with two optical elements (aperture, imaging mirror) and the monochromator/detector system.

The emission spectra were obtained using a 0.5 m scanning monochromator (Acton Research, grating: 1200 g/mm blazed at 150 nm) and a photomultiplier tube (9635 QB Thorn EMI) as detector. The absolute calibration was carried out by comparison with the spectral radiation of a deuterium lamp (V 03, Cathodeon), which was calibrated in units of radiance ($\mu W\ cm^{-2}\ sr^{-1}\ nm^{-1}$) at PTB (Physikalisch Technische Bundesanstalt). The low cut off wavelength for the calibration is 115 nm.

VUV spectra from 115 to 210 nm are presented for a gas flow of 2.5 l min^{-1} of argon with admixtures of xenon and krypton of up to 20%. For the pure Ar discharge, a prevailing Ar_2^* excimer second continuum is observed in the region of 120 to 135 nm, which decreases when Xe or Kr is added to the feed gas. In contrast, the resonant emission of Xenon at 147 nm and of Krypton at 124 nm and especially at 116 nm becomes dominant for a small admixture (0.5 %) of Xe or Kr. For higher admixtures of Xe, the second continuum at 172 nm appears. The recorded spectra between 115 and 180 nm include also several N I emission lines, the O I resonance line and Lyman-α line, due to ambient air. Finally, the integrated spectral distribution is presented in units of $mW\ sr^{-1}\ cm^{-2}$ in dependence on gas mixture and distance to the nozzle. The total emitted optical power is highest for pure Ar gas flow, however, by adding small admixtures of Kr and Xe in particular, the spectral distribution is effectively changed.

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Surface Characteristics and Printing Properties of PET Fabric Treated by Atmospheric Dielectric Barrier Discharge Plasma

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Poly (ethylene tere phthalate) fabric, PET, has been treated using DBD discharge as a type of low–temperature plasma under atmospheric pressure for 1 to 15 minute under different powers ranging between 0.3 to 3 watts. The effects of DBD treatment on the surface of a test PET fabric are examined, reported and discussed. The surface analysis and characterizations were performed using

X-ray diffraction (XRD), Fourier transition infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) before and following the DBD processing.

SEM analysis shows significant surface morphology changes in plasma treated polyester fabric surface while FTIR analysis indicates that the reactivity of the surface was increased. The discharge parameters used are correlated with the changes in the surface characteristics found after DBD processing, of various durations, in atmospheric environment.

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AFM and Contact Angle Investigation of Growth and Structure of pp-HMDSO Thin Films

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HMDSO was plasma polymerized on silicon wafer and polyethylene (PE) substrates. The chemical structure of the pp-HMDSO was analysed with Fourier-Transform Infrared (FT-IR) spectroscopy. The morphological structure of the thin films deposited on the different substrates was investigated by means of atomic force microscopy (AFM), indicating different coverage mechanisms. In order to investigate the growth process of the pp-HMDSO, films of different thickness were also deposited, varying the plasma deposition time from 10 s to 1800 s. Thickness and structure of such deposits was detected with AFM. Finally, hydrophobic characteristics of the different samples was evaluated by means of contact angle measurements and correlated with the morphological characteristics.

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Formaldehyde Abatement by Atmospheric Plasma and Catalyst

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Abatement of formaldehyde by non-thermal plasma produced by direct-current positive streamer corona discharge in multi point-to-plane reactor was studied experimentally. The removal efficiency of formaldehyde and the formation of products were evaluated as functions of the input concentration, the gas flow rate, the discharge polarity and discharge mode. The effects of various pellets placed inside the reactor, in the combination with plasma or without it were investigated. The discharge properties, chemical process and formed by-products were found influenced by the processes of adsorption and plasma-assisted catalytic reactions. Compared to individual treatment by the plasma or pellet catalysts, the improvement of the abatement efficiency was observed for plasma combined with TiO_2 and γ-Al_2O_3, especially at relatively high input energies and long-term operation.

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* * *

Surface Modification of High and Low Density Polyethylene by DBD Plasma

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Contribution evaluates an effectiveness of the polyethylene powder modification in atmospheric DBD plasma. For simulation of larger apparatuses operation (and longer modification time), tested powder batches were repeatedly filled in the discharge channel of the plasma reactor, number of transits through the plasma reactor being one of the investigated parameters.

The wettability of the polyethylene powder was determined with a tensiometer. Powder surface changes were evaluated with XPS and correlation between XPS results and wettability was revealed. XPS results confirm formation of C=O and COOH functional groups on the powder surface after modification. Wettability increase correlates with the O/C ratio changes. Low-density polyethylene modification seems to be more effective than that of high-density polyethylene. Modification effect reduction was remarkably small (max.

reduction about 20% during 500 days after the modification date), hence modification effect is also very time stable.

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* * *

Effects of Different Plasma Source on the Growth of Bacteria

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The sterilization effect of two types of plasma, namely: DC and micro wave (MW) generated plasma was investigated. The effect of irradiation time, working pressure and power (in case of MW plasma) were in particular investigated. Complete sterilization was achieved at irradiation time of 120 sec when DC plasma was used and at 180 sec when MW plasma was used. Neither working pressure nor MW power were observed to induce effect the sterilization process.

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* * *

Photocatalytic Efficiency of TiO_2 Thin Films Deposited by PECVD, PVD and Modified with Addition of Noble Metals

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This review deals with photocatalytic efficiency of TiO_2 thin films deposited by PVD, PECVD and modified with addition of noble metals (Ag, Cu) to its surface taking advantage of Shottky barrier. Basically, the photocatalytic process is initiated by the photogeneration of electron/hole pairs in the semiconductor by photon absorption of UV-light. In photocatalysis the addition of noble metals to a semiconductor can change the photocatalytic process by changing the semiconductor surface properties. When the two materials are connected electrically, the barrier formed at the metal-semiconductor interface called Shottky barrier. After excitation the electron migrates to the metal where it becomes trapped at the Shottky barrier and electron-hole recombination is suppressed.

TiO_2 thin films were deposited on glass substrate by PECVD and PVD and its surface was modified by nanoparticles of silver and copper. In order to study the influence of the metal particles on the photocatalytic efficiency we deposited thin silver (copper) film on top of the TiO_2 films and tempered the system, thereby forming small separated silver and copper

clusters. The photocatalytic activity was evaluated from decomposition speed of aqueous solution of the Orange 7, (sodium salt of sulphonated azo dye), exposed to UV light. The structure of the nanoparticles was examined by SEM, AFM and EFM. The influence of the substrate, tempering and deposition parameters on the resulting properties of the modified films was studied.

A summarization of relations between modified and unmodified films properties, deposition parameters and photocatalytic activity was made.

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* * *

Computational Study of Plasma-Substrate Interaction in Plasma-Assisted Technologies

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The low-temperature plasma is widely used in many technological applications, therefore the detailed description and understanding of physical and chemical backgrounds of these processes is very desirable. Especially the knowledge of properties of plasma surrounding substrates during plasma-assisted treatment of materials is of a great importance for the whole technological process. As the theoretical study is usually limited to very simplified geometries – planar, cylindrical, etc. – the computer simulation was used as a more sophisticated tool for the study of the interaction of chemically active plasmas with immersed metal substrates.

The technique used was the combination of multidimensional fluid modelling and particle simulation codes. The fluid part of our model consisted of continuity equations for all charges species, Poisson's equation and energy balance for electrons. The basic scattering processes were included in the fluid model, too. The particle simulation technique was used in two different ways. First, the non self-consistent particle code with stochastic treatment of collision processes was used for the calculations of electron energy distribution function necessary for the fluid part of model. After finishing the hybrid fluid-particle simulation the pure particle code was used for the derivation of all necessary quantities, which characterise the plasma-substrate interaction.

This approach enabled us to study in detail the structure of the sheath and presheath near metal substrates with realistic geometries and finite dimensions. The main attention was devoted to the influence of substrate geometry in both macroscopic and microscopic spatial scales and to the plasma properties important for treatment on materials. In the contribution the influence of both substrate quality and various plasma parameters as its composition, pressure, etc. on the surface processes on substrates immersed into plasma is analysed.

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Changes of Wool Fibres Properties by Plasma Treatment

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The wool fibre exhibits a typical core–shell structure consisting of an inner protein core (cortex) and surface shell (cuticle). The hydrophobic nature of the cuticle and the high cross-linking density in the outermost fibre surface creates a nature diffusion barrier. That influences wettability, sorption properties and complicates wool finishing processes, such as printing, dyeing or shrink-proofing. Surface modification plays an important role. To date, the required surface modification is mainly accomplished by wet chemical processes using special auxiliaries.

The effects of atmospheric pressure plasma treatment on wool fabric were tested in this study. A Diffuse Coplanar Surface Barrier Discharge (DCSBD) has been used. Pure wool fabric has been exposed to different intensive plasma-treatment (different exposure times at constant conditions).

Changes of fibres surface were characterized by means of IR spectroscopy, XPS and other instrumental methods. The maximum experimental attention was focused to sorption properties. It was tested textiles wettability by the help of Drop Test and Capillary Test. Further, it was observed dye sorption. Wool fabrics were dyed in dye bath by common used acid dyestuffs. As criterions of dye sorption on wool were used dyeing rate and dye uptake on wool fibres. At last, it was carried out printing of wool by acid dyestuffs.

Experiments showed invasion of subsurface layer of cuticle, increasing of hydrophility and thus acid dye adsorption after plasma treatment of wool fibres. Plasma-treatment wool adsorbs dye more intensive on moderate terms (lower temperature). On grounds results of experiments may be stated that plasma treatment of wool can replace wet pre-treatment processes of wool dyeing and wool printing. No usage of water and chemicals in plasma treatment caused that the application of low-temperature plasmas to wool has become of increasing interest. The pre-treatment of wool with low temperature plasmas gives an appropriate environmentally acceptable alternative to conventional treatments.

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Atmospheric Pressure Microwave Microplasma Source

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Nowadays, there is a growing interest in atmospheric pressure microwave microplasma sources (MMSs). They are needed for gas cleaning, microwelding, surface modification, light sources, and atomic spectroscopy system. They can be also used in the biomedical

applications such as sterilization of medical instruments, high-precision surgery, cells treatment and deactivation of bacteria and viruses.

In this work we present a new MMS based on a coaxial line. The main advantage of the presented MMS is its simplicity and low cost.

Experimental setup consists of a microwave magnetron generator (2.45 GHz), microwave power measuring system (directional coupler, power meters with thermistor mounts), gas flow control system (Mass flow controller) and microwave microplasma source (MMS). The whole arrangement was connected via coaxial cable (50 Ω).

The absorbed microwave power P_A, i.e. microwave power delivered to the discharge was calculated as $P_I - P_R$, where P_I and P_R are the incident and reflected microwave powers, respectively. The incident and reflected microwave powers P_I and P_R were directly measured using directional coupler equipped with bolometric heads and HP power meters. The ferrite isolator protected the magnetron head from the reflected microwave power.

Due to the presence of an outer conductor the new MMS exhibited a better impedance matching (the lower reflected microwave power P_R) than the previous model MMS.

In this investigation argon at atmospheric pressure was used as a working gas. The argon flow rates varied from 1 to 20 l/min. The microwave power was from 10 to 80 W.

The temperature of the plasma gas produced by the MMS could be changed by varying the gas flow rate and/or absorbed microwave power. When the gas flow rate increased and/or the absorbed microwave power decreased, the plasma gas temperature decreases. The gas temperature measured on the top of plasma jet could be changed from 30 °C to 1200 °C. The wide range of plasma gas temperature increases the area of the MMS applications.

According to the our investigations we observed that the length and width of the microdischarge increases with increasing gas flow rate and absorbed microwave power. In other words, we can obtain different dimensions of the microdischarge by choosing operating conditions.

The simplicity of the MMS, operation stability and parameters of the microplasma allows the conclusion that the presented MMS can find practical applications in various fields.

* * *

Study of Surface Free Energy of Plasma Treated Polycarbonate

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Recently polycarbonate (PC) become to be one of the most important industrial commodities. Although their unsuitable properties that are connected with low microhardness, scratch resistance, low surface energy and chemical resistivity, degradation when exposed to UV radiation, there is still rising call in using this materials. Economical factors like low prise and cheep processing in comparison with glass for example are the most significant factors in industrial and other applications. One of the most hopeful technologies for elimination of PC disadvantages is Plasma Enhanced Chemical Vapour Deposition (PECVD) of hard thin films. Because of relatively low surface free energy of PC, it is necessary to improve this important factor influencing the film-substrate adhesion. The problem could be solved using plasma treatment of the PC surface before the deposition, what was the main goal of the present work.

The PC surface was modified using low pressure capacitively coupled r.f. discharge. To measure the effect of plasma treatment, surface free energy was evaluated. Evaluation was done with contact angle measurement using at least six liquids, to obtain accurate results of each component (Lifshitz-van der Waals part, electron-acceptor and electron-donor part) of surface energy. Liftshitz-van der Waals/acid-base approach was used as one of the most precise model. Measured dates were determined using multi-linear regression to evaluate them really correct.

The results were compared with the most often used models. For example for OWRK approach and regression evaluation we obtained for pure polycarbonate value of total surface free energy 38.59 with error 5.3 mJ/m^2. Using the LW/acid base approach and regression evaluation we obtained value of total free surface energy of pure polycarbonate 44.89 mJ/m^2 with error 2.85 mJ/m^2.

Significant increase of surface free energy was observed in both LW and acid-base components. The increase of total surface free energy was about 50%. The present work was aimed at observation of change of the surface free energy with experimental conditions, like gas mixture, pressure during treatment process, bias voltage, power, time, and storage time.

The work will be aimed at optimisation of experimental parameters to obtain good adhesion and stability of the substrate-film system and study of change of surface free energy and its components during plasma treatment.

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* * *

Thin Film Deposition Using PECVD

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The electric and the photo characteristics of solar cells were studied at TU-Delft (Holland).The deposition technique that was used is an rf PECVD AMOR deposition system "radiofrequency Plasma Enhanced Chemical Vapor Deposition" on an amorphous thin films that has been deposited on a supporting substrate made from glass. High quality thin films were deposited at temperature of 180°C and an rf power of 4 watts, while CVD "Chemical Vapor Deposition" techniques require higher temperature range to produce similar quality films. Another system is used (Leybold deposition system CVD) for depositing metallic contacts from either silver (Ag) or aluminum (Al). AMOR and Leybold systems were used to deposit devices and layers with different specifications. Two substrates were used for layer; glass-based and c-Si wafer-based while TCO-coated glass substrate was used for devices. Three types of glass-based layers; p, n and i were deposited with 300 nm thickness each. Three 300nm intrinsic layers of c-Si based-wafer were deposited at three different rf powers; 3W, 4W and 5W.On the other hand three devices with three different thicknesses; 150 nm, 300 nm and 450 nm were deposited on TCO-coated substrate. The measured performances of solar cells

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Exposed Charge by Negative Corona Discharge is Dominant Parameter of Staphylococcus Epidermidis Grow Inhibition

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The decontamination of surfaces by pin-to-plane corona discharges was tested directly on agar plates with *Staphylococcus epidermidis* inoculums. The dense inoculums were used; an area untouched by the discharge was coated by a continuous cover of bacterial culture. Areas without bacterial colonies, i.e. zones of bacteria grow inhibition were measured. This method is analogical to testing of antibiotic sensitivity of bacteria; bacterial grow inhibiting factors are discharge products in this case. Hypothesis that inhibition zone dimensions are determined by charge was verified by experiments with variations of discharge current and discharge voltage, but the same exposed charge. A distance between electrodes was changed indirectly by spontaneous agar deformation caused by ionic wind.

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Langmuir Probe Diagnostics of Pulsed Cylindrical Magnetron

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In this paper we present a Langmuir probe study of the cylindrical post magnetron discharge in argon which was powered by pulsed dc power supply.

The system consists of hollow cylindrical anode with diameter of 60 mm and coaxially mounted water cooled cathode with the diameter of 10 mm. The discharge volume is limited by two disc-shaped electrodes to the length of 120 mm. Constant and homogeneous magnetic field has axial direction and is created by couple of water cooled coils. The high-vacuum chamber is pumped by oil-free pumping system consisting of the combination of turbomolecular and piston pump to the ultimate pressure in the order of 10^{-3} Pa. During the discharge operation the argon continuously flows through the system with the flow rate of about 1 sccm.

The pulsed discharge was operated in the pressure range of 1 to 10 Pa and magnetic field below 20 mT where it was stable. The pulse voltage ranged from 600 to 800 V with the duty cycle 100 μs and the repetition period of 1 ms.

Measurements were performed using the cylindrical Langmuir probe mounted on radially movable feedthrough. The probe orientation was perpendicular to the magnetic field to

minimize its effect on electron probe current collection. Probe characteristics were recorded using pc labcard with the sampling rate of 2 Msamples/s and A/D resolution of 14 bit.

We present time-resolved radial dependences of the discharge current, plasma density, electron temperature and plasma potential measured both during the on time of the voltage pulse and in the afterglow phase.

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Corona Discharge Ion Sources for Fine Particle Charging

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Charging of aerosol droplets and solid particles are used in many industrial processes such as electrostatic painting, particle separation and electrostatic precipitation. In most of charging devices, electrical discharges are used as a source of ions, which are deposited onto the particles. For example, in two-stage electrostatic precipitators, which provide an opportunity to increase the particle removal efficiency, the first section is that of particle charging. In the present paper the charging process in an ionic current and alternating electric field was investigated. Alternating electric field charger was used as a charging devices in these experiments. The current voltage characteristics of the electrical discharge in this device, and the charge imparted to the particle were determined. The charging process was also simulated numerically and compared with the measurements carried out for various discharge currents. The photographs of particle trajectory in the charging zone in the presence of electrical discharge were compared with numerical simulations. The level of charge was measured at the outlet of the charger and was compared to the Pauthenier limit for different supply voltage, and frequency. MgO and the fly-ash particles were used in the experiments. It was noticed that higher supply voltage of the electrodes give higher level of particle charge, but at the same time, with the increase of supply voltage, the particle deposition on the charger elements also increased. Therefore the choose of the optimal operating parameters of the charger are very important.

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Investigations of Hollow Cathode DC Plasma Jet System as a Source for TiO_x Deposition

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DC plasma jet system was applied as a source for deposition of TiO_x thin films on plastic and glass substrates. The reactor vessel was constructed in UHV technology in order to achieve very clean and defined experimental conditions. The plasma-jet system consisted of water-cooled titanium nozzle with inner diameter 4 mm. The plasma flow entered the cylindrical reactor vessel 30 cm in diameter and 35 cm in length that was continuously pumped by combination of turbomolecular and an oil-free piston pump. The ultimate pressure in the reactor chamber was in the order 10^{-5} Pa. The experiments were performed at typically 30-70 Pa argon-oxygen pressure, discharge current 100 mA and the mass flow of argon/Ar-O_2 mixture around 100 sccm.

Parameters of the plasma generated by the hollow cathode plasma source were investigated by Langmuir probe diagnostics. We present spatial distribution of electron concentration and electron (effective) temperature as well as of the mean electron energy. Investigations of plasma parameters were performed in two different modes. In the first case the physical admixture of two gases Ar and O_2 was fed directly in to the nozzle of system. In the second case the O_2 entered the reactor chamber directly without passing the powered nozzle. TiO_x thin films were deposited also at these two modes and at different pressures in order to compare deposition speed and thin films properties. Substrates were oriented perpendicularly to the vertical axis of the plasma jet. Deposited layers were investigated by AFM.

Key words: Plasma jet system, deposition, TiO_x thin films, Langmuir probe, hollow cathode, DC discharge.

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Computer Simulation for Optimization of Ion Sources

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Results of the computer simulation for ion sources optimization used for ion implantations had been done. The highly stripped ion source has been designed to provide high current beams of multiply charged Phosphorous and Boron ions for high-energy ion implantation. However, the total current transport is lying in the range about 30%. The modified computer code Cobra has been used to evaluate the extraction and dc-acceleration systems as well as beam transport system and find main channels of ion beam loss and ways for reducing it. The

calculations indicate that the losses of extracted ion beam mainly occur in the transport channel. The computer modelling allows find optimal geometry for ion-optical system. The results of experiments with the modified geometry are support of simulation results. With the optimization of geometries of the ion-optical system and experimental setup, the maximum current transport for Boron ions has been attained.

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Nitrogen-Oxygen Mixture Optimisation in Low Energy Dense DC Glow Surface Conditioning of Titanium

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Samples of pure Titanium have been treated by means a PIII process in a DC glow discharge in pure oxygen and different nitrogen–oxygen mixtures. In contrast with conventional voltage supply based glow PIII, the present study has been conducted on a novel specifically designed high current supply which allows a high electron density to be kept constant regardless gas pressure variations within the operational ranks. Thus, the acquired sample characteristics can be more clearly ascribed to the chemical composition of the mixture. One stratified TiO_2 (rutile) and $TiN_{0.26}$ layer was identified from XRD and Raman spectroscopy, both of these compounds reputedly being highly biocompatible. The superficial hardness of the samples was improved up to more than five times harder than that of the untreated reference sample, namely, up to 1600 HV (10g load) with a 2–6 μm deep implanted layer. These optimal results have been obtained from an 80% nitrogen 20% oxygen mixture at 1×10^{-2} Torr. Furthermore, with this gas proportion, the best roughness finishing of the sample set was accomplished, which can be more relevant for biocompatible applications.

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Features of Materials Alloying Under Exposures to Pulsed Plasma Streams

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It is well known that modification of constructional steels with powerful pulsed plasma streams results in hardening their surfaces and increasing the wear resistance of steel samples. Under the pulsed plasma influence the high speed heating and melting of treated surface, high gradients of temperature arising in the near-surface layer of material contribute to high speed diffusion of plasma stream ions into the depth of the modified layer, structure and phase changes in a surface layer, and formation of the fine-grained or quasi-amorphous structures under the fast cooling of molten layer.

In this paper features of materials alloying from gas and metallic plasma, as well as due to the mixing process in liquid phase are investigated. The experiments were carried out with pulsed plasma gun[1], which generates plasma streams with ion energy up to 2 keV, plasma density $2x10^{14}$ cm^{-3}, average specific power of 10 MW/cm^2 and plasma energy density in the range of (5-40) J/cm^2. The nitrogen, helium, hydrogen and other gases can be used as working gases. The regime of plasma treatment was chosen with variation of both the discharge voltage and the distance of the material surface from the gun output.

Modification of thin (1-2 μm) PVD coatings of Mo, W, Ni, TiAlN, FeB and others as well as the coating mixing with substrate under the pulsed plasma processing are analyzed. For example, after alloying of ferritic/martensitic steel EP-823 with Mo the concentration of molybdenum in modified layer achieved 20 % for single treatment cycle and 30 % after two cycles of processing.

Decrease of grains size (from tens μm to hundreds nm), roughness and porosity were obtained in result of plasma irradiation of thick (~0.1-0.3 mm) plasma sprayed coatings of Co-32Ni-21Cr-8Al-0.5Y, ZrO_2 and Ti64. The modified layer with homogeneous structure and with thickness up to 50 μm was formed in result of plasma treatment.

Mechanisms of surface modification of WC-Co, WC-Ni and other alloys under irradiation with pulsed plasma streams of different ions are discussed. It is shown that pulsed plasma treatment results in essential improvement of physical and mechanical properties of exposed materials.

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Nanostructure of Photocatalytic TiO_2 Films Sputtered at Temperatures below 200°C

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The article reports on correlations between the process parameters of reactive pulsed dc magnetron sputtering, physical properties and the photocatalytic activity (PCA) of TiO_2 films sputtered at substrate surface temperature $T_{surf} \leq 180°C$. Films were deposited using a dual magnetron system equipped with Ti (Ø 50mm) targets in $Ar+O_2$ atmosphere in oxide mode of sputtering. The TiO_2 films with highly photoactive anatase phase were prepared without a post-deposition thermal annealing. The decomposition rate of the acid orange 7 (AO7) solution during the photoactivation of the TiO_2 film with UV light was used for characterization of the film PCA. It was found that (i) the partial pressure of oxygen p_{O2} and the total sputtering gas pressure p_T are the key deposition parameters influencing the TiO_2 film phase composition that directly affects its PCA, (ii) the structure of sputtered TiO_2 films varies along the growth direction from the film/substrate interface to the film surface, (iii) ~500 nm thick anatase TiO_2 films with high PCA were prepared and (iv) the structure of sputtered TiO_2 films is not affected by the substrate surface temperature T_{surf} when $T_{surf} < 180°C$. The interruption of the sputtering process and deposition in long (tens of minutes) pulses alternating with cooling pauses has no effect on the structure and the PCA of TiO_2 films and results in a decrease of maximum value of T_{surf} necessary for the creation of nanocrystalline nc-TiO_2 film. It was demonstrated that nc-TiO_2 films with high PCA can be

sputtered at $T_{surf} \leq 130°C$. Based on obtained results a phase zone model of TiO_2 films was developed.

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Electromagnetic Field Distributions in Waveguide-Based Axial-Type Microwave Plasma Source

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Microwave discharges find applications in technological processes such as purification of gases, abatement of fluorinated compound gases, decontamination of chemical warfare agents. Applying microwave discharges for hydrogen production via hydrocarbons reforming have been reported recently. The hydrogen production becomes an important issue currently, because hydrogen is seen as a promising energy carrier for the next decades.

A waveguide-based microwave plasma source (MPS) for hydrogen production via methane reforming we reported earlier. This MPS allows stable operation at microwave power level from 600 to 6000 W and the gas flow rate from 50 to 200 l/min. The discharge is generated in a quartz tube. The processed gas is introduced to the discharge region by a metallic tube, which length can be changed. The discharge is stabilized by additional gas flow. Two metallic tubes of the gas supplying system are placed in the lower part of the MPS and constitute a coaxial line. A shielding metallic sleeve is placed in the upper part of the MPS coaxially with the discharge tube.

In this paper we report results from simulation of the spatial distributions of the electromagnetic field inside the MPS. The studies were aimed at optimization of discharge processes and hydrogen production. The numerical calculations were performed using FlexPDE^{TM} software, which enables to solve partial differential equations. To avoid problems with discontinuity of the electric field components on boundaries of dielectrics, the magnetic field component distributions were calculated in the first stage. Subsequently the electric field components were determined.

We determined the electromagnetic field distributions for two cases – without and with plasma inside the MPS. For the first case, we examined the influence of the length of the inner conductor of the coaxial line on electromagnetic field distributions. We obtained standing wave patterns along the coaxial line and found resonances for certain positions of the coaxial line inner conductor.

Calculations for the case with plasma inside the MPS were performed assuming that distributions of plasma parameters are known. Simulations were done for several values of maximum electron concentration. We found that for values of electron concentration greater than $3 \cdot 10^{18} m^{-3}$ strong skin effect in the plasma is observed and then the plasma may be treated as an extension of the inner conductor of the coaxial line.

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New Trends in Non-Thermal Plasma Ozone Generation

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First ozone generating system based on the electrical discharge was proposed in 1857 by Siemens. Present efforts in the research of ozone generation are focused on combination of electrical discharges with different additives such as ferroelectric pellets or catalysts in the discharge region with the aim to obtain higher ozone concentrations, higher ozone generating efficiencies and design of more compact and miniaturized ozone reactors.

Corona discharge in air is apart of the source of charged and excited species also the source of ultraviolet radiation. The strongest emissions originate from the second positive system of nitrogen ($C_3\Pi_u \rightarrow B_3\Pi_g$), which emits photons of wavelength 337.1 nm. The first negative system ($B_2\Sigma_u^+ \rightarrow X_2\,\Sigma_g^+$) of N_2^+ emits radiation of the wavelength 391.4 nm.

With the aim to increase the corona ozone production we studied the role of this radiation on discharge ozone production by placing the photocatalyst into the discharge region. An appropriate choice of such photocatalyst should be based on the wavelength of radiation, which activates the photocatalyst. From the wide range of semiconductor catalysts the titanium dioxide TiO_2 suites the best the requirements.

The TiO_2 is a *n*-type semiconductor, biologically and chemically inert. A series of its energy levels is associated with covalent bonds among atoms composing the crystallite (valence band) and a second series of spatially diffuse higher energy levels is associated with conduction in the macromolecular crystallite (conduction band). Both series are strictly separated by a forbidden energy gap of 3.2 eV.

The electron of the valence band of TiO_2 becomes excited when illuminated by UV radiation. Wavelength of the radiation necessary for this photo-excitation is 388 nm. The excess energy of excited electron promotes it to the conduction band of TiO_2 therefore creating the negative-electron (e-) and positive-hole (h+) pair:

$$\mathbf{TiO_2 + hf \rightarrow h^+ + e^-}$$

The electron and positive-hole can react with the molecules in the vicinity of the catalyst. In air the electron reacts with an oxygen molecule to form the superoxide anion O_2^-:

$$\mathbf{e^- + O_2 \rightarrow O_2^-}$$

This cycle continues as long as the ultraviolet radiation is available. In case of negative corona discharge in air the current is sustained by negative ions. The superoxide anions appearing due to the UV irradiation of TiO_2 contribute to the discharge current. It is therefore reasonable to expect, that for particular voltage addition of TiO_2 will increase discharge current. The superoxide anions as well as other radicals should be also added to other plasma components produced by the discharge. All these species in different levels contribute to the processes leading to the discharge ozone production.

In our study we used hollow needle to mesh DC corona discharge with TiO_2 globules on the mesh. The discharge was enhanced by the flow of air through the needle. We found that for the needle biased negatively for particular current addition of TiO_2 catalyst on the mesh electrode drastically increases discharge ozone production.

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* * *

Application of High Velocity Streams of Dense Plasma for the Creating of High Adhesive Compounds of Chemically Noninteracting Metals

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The work presents the experimental results of investigation of the possibility of the creating of high adhesive compound of chemically noninteracting metals by means of pulse streams of high temperature dense plasma. The 4 kJ plasma focus installation was used as a source of pulse streams of plasma. In the experiment assemblies of Cu-W and Pb -Fe samples were used. The deep penetration of atoms Cu and Pb accordingly in W and Fe was found.

The mechanisms of the penetration of chemically neutral atoms into a material of the target can be connected with the following processes: the energy transfer from plasma pulse to implanting atoms, the origin and distribution of shock waves in the material of a target, and also the Rayleigh - Taylor instability of the border of two combining materials.

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* * *

ADBD Plasma Surface Treatment of PES Fabric Sheets

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Plasma treatment of textile fabrics is investigated as an alternative to the environmentally hazardous wet chemical fabric treatment and pretreatment processes. Plasma treatment usually results in modification of the uppermost atomic layers of a material surface and leaves the bulk characteristics unaffected. It may result in desirable surface modifications, e.g. surface etching, surface activation, cross-linking, chain scission and oxidation. Presented paper contains results of the applicability study of the atmospheric pressure dielectric discharge (ADBD), i.e. dielectric barrier discharge burning in air at atmospheric pressure and ambient temperature for synchronous treatment of several sheets of fabric.

For tests sheets of polyester fabric were used.

Effectivity of the modification process was determined with wettability measurements evaluated by means of the drop test. Wettability of individual sheets of fabric has distinctly increased after plasma treatment.

Plasma induced surface changes of textiles were also proven by identification of new functional groups at the modified polyester fabric surface. Existence of new functional groups was detected by ESCA scans. For verification of surface changes we also applied high-resolution microphotography. It has shown distinct variation of the textile surface after plasma treatment.

Important aspect for practical application of the plasma treatment is the modification effect time-stability, i.e. time stability of acquired surface changes of the fabric. Changes of the fabric surface wettability diminish in time and textile hydrophobicity recovers in time after treatment. The recovery of hydrophobicity was fastest in first days after treatment, later gradually diminished until reached original untreated state.

Presentation of this contribution was supported by the Czech Technical University in Prague Research Project No. CTU 0814213.

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Electrohydrodynamic Flow in a Wire-Plate Non-Thermal Plasma Reactor Measured by 3D PIV Method

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Non–thermal plasma techniques have become an important tool for controlling the emission of various gaseous pollutants, such as acid gases (SO_x, NO_x, HCl, etc.), greenhouse gases (CO_x, N_xO_y, para–fluorocarbons, etc.), ozone depletion gases (freons, halons, etc.), volatile organic compounds (VOCs, e.g. toluene, xylene, etc.) and toxic gases (Hg, dioxins, etc.). The main advantages of the non–thermal plasma techniques are small space volume, low cost, high pollutant removal and energy efficiencies.

This work was aimed at measurements of the electrohydrodynamic (EHD) secondary flow in a wire-plate non–thermal plasma reactor using three-dimensional Particle Image Velocimetry (3D PIV) method. Collecting such data is important for designing non–thermal plasma reactors of high performance efficiency.

The wide-type non–thermal plasma reactor used in this work was an acrylic parallelepiped with a wire discharge electrode and two plate collecting electrodes. The wire electrode (diameter 1 mm, length 200 mm) was placed perpendicularly to the main flow, in the middle of the reactor between the plate electrodes, which were placed on the top and bottom of the reactor. The width of each plate electrodes was 200 mm, while the plate-to-plate electrode spacing was 100 mm (i.e. the width to height ratio was 2:1 in the reactor). Air flow seeded with a cigarette smoke was blown along the reactor duct with an average velocity that could be varied from 0 to 0.9 m/s. The positive DC voltage was applied to the wire electrode through a 10 MΩ resistor. The collecting electrodes were grounded. The applied voltage was varied between 0 and 30 kV. The 3D PIV velocity fields measurements were carried out in four parallel planes stretched along the reactor duct, perpendicularly to the wire electrode and plate electrodes. The first plane was placed in the reactor centre when the other were placed 60 mm, 20 mm and 10 mm from the side wall.

The measured flow velocity fields illustrate complex nature of the EHD induced secondary flow in the non-thermal plasma reactor. In the plane placed in the reactor centre the mean flow is almost two-dimensional in terms of time-averaged observations. However, the analysis of instantaneous EHD flow images and velocity fields showed that the EHD flow is

very turbulent. In the other three measured planes the flow was also very turbulent and even time-averaged flow velocity fields show 3D structures caused by the side-wall effect.

The results show clearly 3D character of the EHD secondary flow, resulting from the 3D interaction of the electric field, electric charge and the main gas flow in the non-thermal plasma rector. Even in wide non-thermal plasma reactor the EHD flow can not be assumed to be 2-dimensional when its short-time behavior is considered.

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* * *

Influence of Dielectric Barrier Discharge Treatment on Adhesion Properties of Platinum Coated PP and PET Fabrics

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Low temperature plasma treatment has been conducted in textile industry and has some success in the dyeing and finishing processes.

In this paper, an attempt was made to apply low temperature plasma treatment to improve the adhesion property of Polyethylene terphtalate (PET) and Polypropylene (PP) fabrics.

PP and PET fibers have been increasingly used in textile industries for a variety of applications ranging from filtration, composites, and tissue engineering and electronic textiles. The surface properties of these polymer fibers are of importance in various applications. The surface properties of PP and PET fibers can be modified by different techniques.

This paper is aimed at understanding the basic properties of platinum-deposited PP and PET fabrics after treating with low temperature plasma treatment. Atmospheric plasma treatment was employed in this paper to activate and etch surface.

In this research work, the PP and PET fabrics were treated by Diffuse Coplanar Surface Barrier Discharge for up to 10 minutes, and both treated and untreated samples were coated with platinum.

The textile properties of plasma-treated-Pt-coated polypropylene and polyethylene terphtalate fabrics and untreated-Pt coated fabrics were evaluated by different standard testing methods in terms of both physical and chemical performances.

The washing and rubbing fastness were investigated according to standards methods. The morphology changes of fabrics after plasma treatment were characterized by scanning electron microscopy (SEM).

X-ray photoemission spectroscopy (XPS) and Furrier Transform Infrared (FTIR) analyses revealed chemical surface modifications occurring after the plasma treatments.

For testing the quantity of Platinum on the samples the Spectrophotometer were used to investigate the Reflective properties and the LIBS (Laser Induced Breakdown Spectroscopy) method was used as well.

And the conductivity of samples was measured.

The study showed that adhesion of the Platinum to the PET and PP fabrics was greatly enhanced by the air plasma treatment.

The details will be discussed in full paper.

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* * *

Carbon-free SiO_x Films Deposited from Octa-methylcyclotetrasiloxane by an Atmospheric Pressure Plasma Jet

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Thin films produced by plasma-assisted deposition of silicon-organic compounds have found a broad spectrum of applications. According to the varying chemistry of the film material, applications stretch over a wide range from polymer-like films with applications as corrosion protection to quartz-like (SiO_2) films with applications as barrier coatings or to increase the scratch resistance of polymers.

Gradient films with varying chemical composition over the film height are of particular interest to provide both, a good adhesion to the (often polymeric) base material and a satisfactory film density. Another request raises from the deposition of multilayer films, a sequence of films with alternating organic-inorganic composition, e.g. for superior gas permeation barriers. For process simplicity, it is preferable to deposit these films out of one raw material by a controlled variation of the deposition conditions.

While the deposition of polymer-like films with a high organic content is easily accomplished under normal pressure conditions, the production of pure SiO_2 films represents a challenge as silicon oxide (SiO_x) films produced out of silicon-organic molecules often exhibit a high inherent carbon content, compared to films deposited under vacuum.

In the present work, the deposition of carbon-free, quartz-like (SiO_2) films with a non-thermal, RF capillary jet at 27.12 MHz at normal pressure is demonstrated. The jet geometry of the plasma source is specifically appropriate for local surface modification or coating of 3-D objects.

The gas mixture for film deposition is constituted of argon, oxygen and small admixtures of octamethycyclotetrasiloxane (OMCTS, $Si_4O_4C_8H_{24}$). OMCTS has been selected for providing the film precursor due to its favourable element ratio in the molecule compared to other silicon-organic compounds (Si/C=1/2) and the resemblance of its molecular structure on the SiO_2 network unit.

The parametric study reported here focuses on the optimization of the deposition process with regard to the chemical and morphological surface properties of the coating by varying the oxygen feed gas concentration and the substrate temperature.

Surface analysis of the deposited films reveals their exceptionally low carbon content. The XPS signal remains well below detection limit, which is estimated to 0.6 % (XPS atoms).

The film morphology is characterized by means of scanning electron microscopy (SEM) and the chemical composition of the films is analysed by FTIR microscopy and XPS. The analysis of the optical modes of vibrational states of Si-O structures in the FTIR spectrum helps to explain the observed correlation between the structural properties obtained by SEM and FTIR spectra. The nature of the optical modes (longitudinal or transversal) present in the film is enlightened by comparison of attenuated total reflectance spectroscopy (ATR-FTIR) and infrared reflection absorption spectroscopy (IRRAS-FTIR). This information is directly linked to the structural properties of the larger molecular network observed by SEM and displays a consistent image of the dependence of the deposition parameters on the studied films.

* * *

Pulsed High Voltage DBD Reactor for Methane Cracking at Atmospheric Pressure

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Hydrogen is a promising energy vector and methane cracking is a suitable method for H_2 production. However it could become a realistic and believable energetic alternative for humanity when it will be produced from clean and renewable resources. Especially, hydrogen production should reduce the greenhouse gas emissions (like CO_2) to avoid global warming and climate changes.

Most hydrogen is currently produced from the catalytic conversion of natural gas (about 95% methane) at the temperature range 750 - 850 °C and pressure range 3 - 25 atm.

In our work, we propose a method for hydrogen production based on plasma technologies with the aim to lower the gas temperature, the pressure and to increase the conversion efficiency of hydrocarbons to hydrogen by minimizing the energy consumption.

The non-thermal atmospheric plasma is generated by a pulsed *dielectric barrier discharges* (DBD) using different mixtures of methane (CH_4) and argon (Ar). The DBD plasma is powered by a high voltage (1-30 kV) pulsed generator. The pulse width is 10 ns and repetition rate up to 100 kHz. High voltage pulses are an effective method to produce spatially homogeneous, non-equilibrium plasma with a high concentration of radicals and excited particles, which is necessary for effective conversion to hydrogen.

A separate vacuum system has been built to sample the gas from the reactor at atmespheric pressure down to low pressure to be analyzed by quadrupole mass spectrometer.

The cracking products will be detected and quantified by an on-line gas chromatography system.

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Bold Deposition of Hydrophobic Protective Layers on Wood in Surface Discharge at Atmospheric Pressure

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Like other biological materials, wood is susceptible to environmental degradation [1]. Interaction of wood with water can lead to dimensional instability and accelerated bio as well as weathering degradation. Because of this, the surface of wood has to be protected to prolong its durability. Besides of paints, the plasma deposition is very suitable technique for protection of wood surface. Majority of tests have been performed at low pressure, however these processes are very cost consuming. Similar effect can be achieved using the plasma treatment at atmospheric pressure.

By choosing a suitable composition of discharge gas, the hydrophobic surface properties of wood can be obtained. In presented study, plasma assisted deposition of hydrophobic coatings was performed directly on the surface of poplar veneer by surface barrier discharges at atmospheric pressure from the mixture of nitrogen containing HMDSO vapors.

Surface properties of plasma treated wooden samples were studied using the sessile droplet technique to identify surface free energy of treated and untreated samples. The chemical composition of the films was studied by FTIR technique. The colorimetric parameters as whiteness, yellowness and brightness of samples were also studied.

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Optical, Photo-Electrochemical and Photocatalytic Properties of Nanostructured TiO_2 Films Prepared by High Power Pulsed Magnetron

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Due to good technological properties, e.g. high adhesion, hardness, refractive index, transparency, high dielectric constant, semiconducting properties etc., titanium (di)oxides are widely studied as coating material. The most interesting feature of titanium dioxide is its photocatalytic property which can be used as self-cleaning and anti-fogging films or can cause degradation of organic molecules. Titanium oxides can be used as photovoltaic layers,

barrier layers in electronics, too. According to the literature TiO_2 has three crystalline phases: anatase (tetragonal), rutile (tetragonal) and brookite (orthombic). The anatase crystal structure is known to have higher photocatalytic activity compared to rutile, due to its larger band-gap (anatase ~3.2 eV, rutile ~ 3.0 eV). The photocatalytic activity can be improved by doping. Mostly titanium dioxides deposited by classical magnetrons are amorphous and post-deposition thermal annealing is necessary for crystallization. However, this way of thermal annealing is unsuitable for deposition on plastic or thermal sensitive materials.

Our investigation was focused on study of optical, photo-electrochemical and photocatalytic properties of crystalline TiO_2 thin films. The thin films were prepared directly without post-deposition thermal annealing by high power pulsed magnetron operated at repetition frequency 250 Hz. Mean discharge current I_m reached values about $I_m \approx 600$ mA while measured peak current in active part of pulse was much higher $I_p \approx 40$ A. The deposition process was controlled through two independent parameters: pressure in the chamber p and gas composition given by O_2/Ar mixture ratio. Under such conditions the layers were prepared directly in rutile or anatase phase without post-thermal annealing.

Spectroscopic ellipsometry (SE) was employed for investigation of optical constants (film thickness, refractive index n and extinction coefficient k) of deposited TiO_2 in anatase and rutile phase. The measurements were done using a spectroscopic phase modulated ellipsometer (Jobin-Yvon UVISEL) working in a photon energy range from 1.8 eV up to 4.5 eV. Polarization curves and photocurrents were performed using a three-compartment electrochemical cell with a Pyrex Windows. All polarization curves were recorded during 4s/4s intervals of UV radiation/dark period (intensity 1.63 $mW.cm^{-2}$ with maximum wavelength 365 nm). The photocurrents were measured using Heka PG-310 potentiostat and incident-photon-current conversion efficiency (IPCE) was calculated by standard ways.

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Structure and Mechanical Properties of Al-Si-N Films with a Low and High Si Content

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The contribution reports on properties of Al-Si-N films with a low (≤10 at.%) and high (≥25 at.%) Si content reactively sputtered using a closed magnetic field dual magnetron system operated in ac pulse mode. The films were sputtered from composed target (a Si plate fixed by an Al ring with inner diameter $Ø_i$ = 15 or 26 mm). Main attention was devoted to the investigation of a relationship between the structure of the films and their mechanical properties, thermal stability of hardness, and oxidation resistance. The structure and elemental composition of the Al-Si-N films were characterized by XRD and XRF or RBS. Mechanical properties were measured using microindentation and oxidation resistance was tested using TGA in flowing air. It was found that (1) while the films with a low (≤10 at.%) Si content are crystalline (c-(Al-Si-N)), those with a high (≥25 at.%) Si content are

amorphous (a-(Al-Si-N)), (2) both groups of the films exhibit (i) high values of hardness H=21 and 25 GPa and of the oxidation resistance 950°C and 1150°C ($\Delta m \approx 0$ mg/cm^2), respectively, (3) the hardness of a-(Al-Si-N) does not vary after annealing for 4 hrs at 1100°C in air and (4) a high oxidation resistance of c-(Al-Si-N) film with a low (≤10 at.%) Si content is due to the formation of a densified Al_2O_3 surface layer which prevents the fast penetration of oxygen into bulk of the film.

* * *

Formation of Crystalline Al-Ti-O Thin Films and their Properties

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The article reports on the effect of doping of thin Al_2O_3 films with Ti on their structure, mechanical properties and oxidation resistance. The main aim of the investigation was to prepare crystalline Al-Ti-O films at substrate temperatures $T_s \leq 500$ °C. The Al-Ti-O films were reactively sputtered from a composed Al/Ti target of 116 mm in diameter. The amount of Ti incorporated into the Al-Ti-O films was controlled by the diameter $\varnothing_{\text{in Ti}}$ of the hole in the Ti target. The magnetron was supplied with a pulsed dc power supply operated with the repetition frequency f_r=50 kHz. Properties of the sputtered films were characterized using the following techniques: X-Ray diffraction (XRD), X-ray fluorescent spectroscopy (XRF), microhardness testing using a Fischerscope H 100 system and thermogravimetric analysis (TGA). It was found that (1) the addition of Ti stimulates the crystallization of Al-Ti-O films at lower substrate temperatures T_s, (2) Al-Ti-O films with a nanocrystalline cubic γ-Al_2O_3 structure, hardness $H \approx 25$ GPa and zero oxidation (Δm=0 mg/cm^2) in flowing air up to ~1050 °C can be prepared already at low substrate temperature T_s=200 °C and (3) the crystallinity of Al-Ti-O films at a given value of T_s improves with the increasing amount of Ti incorporated in it. The last finding is in a good agreement with the thermodynamically equilibrium binary phase diagram of the TiO_2-Al_2O_3 system showing that the temperature corresponding to the transition between the amorphous and crystalline Al-Ti-O films decreases with the increasing amount of Ti.

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Plasma Treatment of Kevlar and Nomex

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This paper is focused on plasma application on fibers of Kevlar and Nomex. These fibres are typical species of aromatic polyamide. They assert the using in large field – reinforcing of composites, reinforcing of tires, bulletproof application and so on. Most of these applications

require special characteristics of fibre surface. There is discussed the influence of plasma on above-mentioned fibres.

Fibers of Kevlar and Nomex were treated by means of the plasma source of Diffuse Coplanar Surface Barrier Discharge (DCSBD). Flocks of fibres were exposed to plasma ranging from 2 to 5 minutes. In this case the air was the operational gas. Generated discharge had the frequency 15 Hz and the power was 300 W.

The structure and the appearance of fibres surfaces before and after plasma treatment was observed with using of scanning electron microscope (SEM) on device VEGA. The alternative method to value fibre surface is infrared spectroscopy. For this analysis we used device FT-IR Spectrometer One by Perkin Elmer – ATR Technique on ZnSe crystals.

Chemical changes of fibre surface after application of plasma in the air and in argon are only slight. Essentially greater changes we reached by plasmatic polymerization vinyltriethoxysilane at the surface of Kevlar. Here is formed layer of organosilicious polymer with evidently different properties. Alongside plasma treated materials was studied wetting by model liquids with known surface energy and was evaluated surface energy of treated fibers. Surfaces of treated fibers will be analysed by the help of other methods.

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Small Ozone Sterilizer

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The paper presents the results of recent experimental methods of sterilization of microorganisms and the device with the use of ozone and ultrasound. The main aim was to optimize the process of sterilization in small water solution taking into account the ozone concentration, the power of ultrasonic emitter and the temperature of water.

In the present work, the ultrasonic cavitation with simultaneous ozone generation has been used. The high ozone concentration in water solution was achieved by the two-barrier glow discharge generated at atmospheric pressure and a cooling thermo-electric module. Such a sterilizer consists of ozone generator with the pre-ionization in a shape of flat electrodes covered with dielectric material and a high-voltage pulsed power supply of 20 W. The sterilization camera (0.5 liter) was equipped with ultrasonic source operated at 50 W. The experiments on the inactivation of bacteria of the Bacillus Cereus type, E-coli, yeasts et.al., were carried out in the distilled water saturated by ozone. The ozone concentration in the aqueous solution was 9 mg/l, whereas the ozone concentration at the output of ozone generator was 25 mg/l. The complete inactivation of spores took 15 min. Selection of the temperature of water, the ozone concentrations and ultrasonic power allowed to determine the time necessary for destroying the row of microorganisms.

* * *

Deposition of Thin Films in Atmospheric Pressure Homogeneous Discharge

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The atmospheric pressure homogeneous dielectric barrier discharge was used for the deposition of thin organosilicon polymer films. The discharge was burning in pure nitrogen used as a carrier gas and a small admixture of hexamethyldisiloxane (HMDSO), which was used as a monomer. It was assumed that the elevated temperature of the substrate could be the cause of higher film hardness, so the substrate temperature was elevated to the range 45–120 °C. The homogeneity of thin films was enhanced using movable upper electrode, which was moving with the speed 7 $cm.min^{-1}$ above the substrate. High voltage of 12 kV with the frequency 10 kHz was used for the discharge generation.

The mechanical properties of thin films were investigated by means of the depth sensing indentation (DSI) technique using a Fischerscope H100 tester equipped with the Vickers indenter, microscope and CCD camera. This tester enables to register the load and the corresponding indentation depth as a function of time for the loading and unloading processes. Several tests were made at the different maximum indentation loads (i.e. several different indentation depths) to eliminate the influence of the substrate. The composition of deposited films was studied by XPS by means of an ADES 400 VG scientific photoelectron spectrometer using an Mg K_α (1253.6 eV) photon beam at the normal incident angle.

Thin films were deposited on two types of the substrate (glass or silicon) at various temperatures of the substrate (25 °C, 45 °C, 60 °C, 85 °C and 116 °C). The microhardness of the thin film deposited at substrate temperature 25 °C was about 0.5 GPa and the elastic modulus was about 15 GPa. The thin films deposited on silicon at the substrate temperatures 85 °C and 116 °C recorded the best mechanical properties: the microhardness was higher than 4 GPa and the plastic hardness was more than 5 GPa. However, the thin films deposited on glass at the substrate temperatures 116 °C showed the microhardness of 1.3 GPa only.

The results of the atomic composition obtained by XPS show that the carbon content in the film decreases with increasing substrate temperature and the silicon content increases with increasing substrate temperature. However, the films obtain still large content of carbon and nitrogen. The addition of N_2O to the working gas mixture can decrease the carbon content and cause almost stochiometric composition of silicon and oxygen, but the carbon content is still between 10 and 20% and the film microhardness is between 2 and 3 GPa only. This effect of N_2O was observed at temperatures below 40 °C only. At higher temperatures the addition of N_2O inhibits from the film growth.

The refractive index at different samples was changing from 1.55 to 1.57 (measured at 500 nm). Thin films were transparent in visible range.

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Silver Thin Film Deposited by Plasma Focus Device

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Plasma Focus device (PF) has been successfully used as a pulsed ionizing radiation source for many applications: pulsed neutron activation analysis, X-ray source for lithography and radiography, highly energetic ion source for processing of materials in the form of thin films or surface modification. All the radiation is produced at the high-current discharge in a vacuum chamber filled with various gases at pressure of a hundreds Pascals. The sort of radiation depends on the type of gases inside the reactor, material of electrodes, geometry and other parameters. For this reason, PF can be well fitted to a various applications, in spite of the fact that a quite complicated picture of physical processes ruling a generation of radiation still is not understood completely.

In this work we present the results of silver thin film deposition on stainless steel using the PF device.

Stainless steel is used to produce of implants and surgically instruments. Stainless steel is easier to settle by bacterial than titanium, which is used to produce medical devices, but stainless steel is less expensive than titanium. For this reason problem of protection of surface of stainless steel against its settle by bacterial is important.

Silver is know as material of high antibacterial activity. Silver is characterized by high toxicity for cellular with S-H group in cellular wall. This group is in many bacterial genus but is absent in cellular wall in human cellular. For this reason silver is danger for bacterial but not danger for human body.

In this work we present the results of silver deposition on stainless steel surface by PF device. We show that:

- nano-structure of deposited film depend from process parameters,
- antibacterial activity depend from nano-structure of silver film.

* * *

Role of Neutral Gas Temperature on Hysteresis Behaviour of Reactive Sputtering Deposition Process

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Deposition of thin films by magnetron sputtering is nowadays largely used process in many industrial applications. To predict the outcome of the reactive sputtering deposition process one need a model which takes into account major processes taking place in the deposition chamber. Since the working pressure is low (usually less than 1 Pa), the heterogeneous reactions are dominant and determine the general behaviour of the whole deposition process. The model well describing the experimentally observed hysteresis behaviour was developed

by S. Berg and is usually referred to as Berg's model. Moreover, this model states very interesting predictions. However, it has a little drawback. It assumes that the current density is uniform over the whole target area and it does not take into account the gas rarefaction effect.

However in the magnetron configuration the discharge current density is laterally very non-uniform due to the presence of the magnetic field. In front of a magnetron cathode high density plasma is formed in a form of toroid. The central part of the target and its edges are substantially less sputtered than the racetrack part of the target. The original Berg's model was modified in order to accommodate the non-uniformity of the discharge current density. In enables us to derive the lateral variation of the target composition as a function of various process parameters.

Metallic atom leaves the cathode with non-negligible kinetic energy of few eV and after that, it travels certain distance before it impacts on a sample and form a growing thin film. At low pressures (typically below 0.1 Pa), the sputtered atom undergoes few if any collisions with the buffer gas atom. At higher pressures (typically above 1 Pa), it becomes more likely that sputtered atoms collide with the atoms of the buffer gas. At these conditions, the significant part of their kinetic energy is shared with the buffer gas atoms, resulting in both cooling of the sputtered atoms and heating of the background gas. The increase of the gas temperature affects the reactive sputtering due to the simultaneous effect of reactive gas rarefaction and increase of the thermal velocity of the gas species. Both altogether influence the flux of reactive species towards the target and the substrate. We have modified the original Berg's model in order to accommodate the gas rarefaction effect. In our approach, we assumed different temperatures near the target and near the reactor walls. It enables us to derive the hysteresis curves for various temperature conditions in the reactor. If the temperature at the target is higher, the whole hysteresis region is shifted towards higher rates of the reactive gas supply. In this case, the width of the hysteresis curve is not affected. On the other hand increasing the temperature at the substrate results is reduction of the width of the hysteresis curve and consequently in a stabilisation of the sputtering deposition process. It is caused by a shift of the transition from the metallic to the compound mode towards lower reactive gas supplies keeping transition from compound to metallic mode unaffected.

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Surface Modification of Cu-Mo Electrodes by Arc Discharge

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The composite materials Cu-Mo with additions of Co and Fe were used in this investigation. Effects of these elements added in the composite materials on electrodes secondary structure were studied. The state of the electrodes surface has been investigated by optical and electron microscopy (Neophot, Superprobe).

The arc was ignited in air between the end surfaces of the non-cooled electrodes. We used the next parameters of electric arc: the diameter of the rod electrodes was 6 mm, the arc discharge gap was 8 mm and arc current was 30 A.

The metallographic analysis of working layers of a Cu-Mo composition has shown formerly that under influence of a heat flow from the arc discharge in air at current of the order of 100 kA in a working layer the secondary structure is formed. It represents a layer of a variable composition with high-melting peel in the vicinity of a surface.

Some another kind of secondary structure formation is observed in the composite materials Cu-Mo with addition of Co and Fe treated by plasma of free burning electric arc in air at current of 30 A.

Since the input power was less of some orders of magnitude than in our previous experiments, we have the soft eutectic on the molybdate base which is crystallized in a plate form. Because of interacting with oxygen of air the molybdenum oxides are formed which have the high saturation pressure. These oxides at high temperature are intensively evaporated. So the hollow spaces are formed in plates of molybdate.

Observed peculiarities of secondary structure in the working layer of electrodes are realized just in composition materials with additions of elements of VIII series (Co or Fe). Therefore one can conclude that such kind of secondary structure formation is probably caused by these elements.

So, it was found that the electrode working layers are uniquely modified in such mode of electric arc operation. The type of secondary structure is depended from composition of electrode material and discharge-current magnitude as well.

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* * *

Measurements of Ion Flux to the Deposition Substrate in Pulsed Discharges

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The ion flux to the deposition substrate was studied in pulsed DC hollow cathode plasma jet and pulsed DC magnetron deposition systems.

The ion bombardment of substrate is used in plasma depositions of thin films to modify their properties, such as films' structure or surface morphology. The substrate is usually negatively biased to induce the bombardment with positive ions from the plasma. When a dielectric layer is deposited or a dielectric substrate is used, the negative bias is achieved by applying radio-frequency (RF) voltage to the substrate through a blocking capacitor.

A knowledge of ion flux to the substrate is essential to control the deposition process and reproduce the parameters of layers. In this work, the ion flux was measured for substrate bias of different frequencies: 500 kHZ – 13.56 MHz. Two methods to determine the ion flux from the current and voltage measurements on the power feed line to the substrate were used. In the first method, the ion flux was determined from the discharging of the blocking capacitor as the RF voltage was periodically turned off. In the second method, the ion flux was calculated from the current to the substrate at the time, at which the simultaneously measured

voltage on the substrate reached its minimum and the displacement current through the sheath around the substrate was zero. In this method a continuous RF bias can be used.

A dependence on the average, negative DC value of the substrate bias, and on the discharge conditions, such as discharge current or duty cycle, was studied. The ion flux measured in the pulsed discharges was compared with the ion flux measured in the continuous operation. Pulsed mode of discharge excitation has advantage of the higher average deposition rate in comparison with the DC mode.

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Study of PECVD Method for Thin Film Deposition on 3D Substrates

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This paper is aimed on use of PECVD method for thin films deposition on geometrically complicated 3D substrates. Active particles penetration into shielded places of substrate is key presumption for study.

The special model substrate was composed for this work. Quantifying of active particles penetration into the closed slot and other shielded places of substrate was possible due the model substrate. Penetration ability was investigated firstly for simpler molecules – C_2H_2. Plasma polymerization thin film was deposited on model substrate. Experiments with complex molecule Titanium (IV) iso-propoxide (TTIP) were lead in second part of work. TTIP was used as precursor for deposition of thin films based on TiO_2.

Deposited processes used both precursors was simulated by mathematical model. The drift-diffusion type model has been created and the set of differential equations was solved by finite element method (FEM).

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Plasma Polymerization of the $P_3N_3Cl_5N(CH_3)[Si(CH_3)_3]$

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Studied compound $P_3N_3Cl_5N(CH_3)[Si(CH_3)_3]$ is derived from a cyclic phosphazene $P_3N_3Cl_6$. In the mentioned molecule are several potential places for substitution reactions, namely all chlorine atoms and easy removable trimethylsilyl group $Si(CH_3)_3$. Besides, the phosphazene skeleton consisting from phosphorus and nitrogen atoms could be polymerized thermally or in a plasma discharge. Our work was aimed on investigation of reactivity and identification reaction products of the $P_3N_3Cl_5N(CH_3)[Si(CH_3)_3]$ in plasma glow discharge.

Experiments were done in a static and dynamic vacuum. Pressure of argon was 20 Pa, generator output power 50 W, frequency 10 Hz and 50 % duty cycle.

Reaction products were identified by common spectroscopic methods ^{31}P-NMR, LDI-TOF MS and IR spectroscopy. It was found, that acting of plasma on the $P_3N_3Cl_5N(CH_3)[Si(CH_3)_3]$ led in the first stage to condensation on compounds like $P_6N_8Cl_{10}SiC_2H_{12}$. Further reaction caused fragmentation of products on smaller molecules, including destruction of the phosphazene skeleton.

Removing of volatile compounds released during reaction by the dynamic vacuum increased reaction rate and accelerated transformation of $P_3N_3Cl_5N(CH_3)[Si(CH_3)_3]$ to nitridic compounds.

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Removal of Paper Microbial Contamination by Atmospheric Pressure DBD Discharge

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An important part of our cultural heritage consists of paper materials, which are stored in archives and libraries. Paper due to the influence of wide range of agents undergoes different degradation processes that result in alarming conditions of most of the historical documents. One of the serious problem, besides the paper oxidation and acidification, is its microbial contamination. The Analysis of Czech National Library in Prague proved presence of at least 80 different microorganisms in paper documents. Generally, the material sterilization can be achieved by chemical and/or physical means, such as heat, chemical solutions, gases and radiation. Most conventional sterilization techniques are associated with some level of damage to the material or medium supporting the microorganisms. It is therefore desirable to focus the research activities on the new techniques, that are both efficient in microorganism removal and gentle to the medium supporting the microorganisms.

This contribution presents results of the removal of the microbial contamination from paper material using the plasma treatment at atmospheric pressure. Aspergillus Niger, the fungi

commonly found in libraries and archives, has been chosen as a bio-indicator enabling to evaluate the effect of plasma assisted microbial inactivation. Dielectric barrier discharge (DBD) operated at atmospheric pressure was used for the paper sterilization because of its easy applicability for archive prints. This technique has also advantage in low cost of process as the expensive vacuum pumping equipment is not necessary and high reactant concentrations make sterilization process very fast.

Certain amount of fungi was spread on Whatman paper no. 1 and it was cultivated on wort agar plates. Afterwards the dried paper samples were treated in DBD performed in pure nitrogen or argon. The treatment time and the plasma power density were varied in order to see the effect of the plasma treatment on the fungi removal. After the treatment, the microbial abatement was evaluated by the standard plate count method. This proved a positive effect of the DBD plasma treatment on fungi removal. Nevertheless, optimisation with regard to different microorganisms and kinds of papers must be considered.

Moreover the influence of the plasma treatment on the paper properties (colour, paper strength, pH, etc.) was investigated.

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Ambient Air-Plasma Cleaning and Activation of Flat Aluminium Surfaces

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Coatings and adhesive bondings of aluminium are extensively used in the automotive, aerospace and architectural sectors. Traditionally, solvent degreasing, and acid pickling or alkaline etching followed by conversion coating, or anodising treatment, have been used to prepare aluminium surfaces for painting or adhesive bonding. The use of organic solvents and aggressive chemicals presents both health and environmental concerns. An alternative that is safe for both people and the environment is a low temperature plasma cleaning. The plasma surface cleaning make possible the use of waterborne coating solutions having good operability and properties to environment.

The paper will present results on a novel atmospheric-pressure ambient plasma cleaning of aluminium surfaces based on the use of Diffuse Coplanar Surface Barrier Discharge (DCSBD). The DCSBD plasma sources generate thin (~ 0.5 mm) layers of diffuse non-equlibrium plasma of an extremely high plasma power density of some 100 W/cm^3, which results in plasma cleaning times on the order of one second. The plasma treated samples were analyzed by AFM, ellipsometry, and surface energy measurements. The results bring a better understanding of the adhesion of polymer coatings on plasma treated aluminium foil.

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Low-Cost Atmospheric-Pressure Plasma Cleaning and Activation of Glass Surfaces

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Freshly cleaned glass surfaces have a high surface energy and are well wettable. They, however, have a tendency to adsorb organic contamination from the ambient environment. This may lead to non-uniform glass coatings, in particular if deposited from liquid media as in the case of widely used sol-gel coatings, silane coupling agent coatings, electroless metal plating, as well as in jetting fluid dispensing technology that is gaining popularity in the manufacture of flat panel displays.

In any glass coating process, a desired chemical substrate is immobilized on the clean glass surface. This is usually carried out using SiOH groups, which are freely available on the clean glass surface. As a consequence, to obtain a sufficient number or density of modifying agents, beside the glass cleaning also the number of reactive SiOH groups must be increased, i.e., the glass surface must be activated.

The paper will present results on a novel atmospheric-pressure plasma glass cleaning and activation method based on the use of Diffuse Coplanar Surface Barrier Discharge burning in ambient air, nitrogen, and some other low-cost gas mixtures.

The plasma treated samples were analyzed by SIMS, MALDI, AFM, and surface energy measurements. The results obtained indicate that as for the cleaning energy efficiency and speed the method is superior to other similar method based on the use of volume dielectric barrier discharges and plasma jets.

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Plasma-Induced Graft-Polymerization of Polyethylene Glycol Acrylate on Polypropylene Substrates

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A detailed study of argon plasma-induced graft-polymerization of polyethylene glycol acrylate (PEGA) on polypropylene (PP) substrates (membranes and films) is presented. The process consists of four steps: a) plasma pre-activation of the PP substrates; b) immersion in

a PEGA solution; c) argon plasma-induced graft-polymerization; d) washing and drying of the samples. Influence of the solution and plasma parameters on the process efficiency, evaluated in terms of amount of grafted polymer, coverage uniformity and substrates wettability, is investigated. The plasma-induced graft-polymerization of PEGA is then followed by sample weighting, water droplet adsorption time and contact angle measurements, attenuated total reflection infrared spectroscopy (ATR-IR) and atomic force microscopy (AFM) analyses. The stability of the obtained thin films was evaluated in water and in Phosphate Buffer Saline (PBS) at 37°C. Results clearly indicates that plasma-induced graft-polymerization of PEGA is an excellent methodology for anti-fouling surface modification of materials.

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Interaction of Plasma Deposited Polyacrylic Acid Thin Films with Water and Phosphate Buffer Saline

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We deposited thin films from acrylic acid (AAc) vapors mixed with Ar by Radio Frequency (RF) plasma-enhanced chemical vapor deposition (PE-CVD) on a polypropylene (PP) substrate. We improved the deposition process in order to obtain stable coatings after soaking in water at room temperature and in Phosphate Buffer Saline (PBS) at 37°C. The stability was investigated on coatings obtained varying the RF power input and keeping constant the other relevant operating parameters: total pressure, Ar and monomer flow rate and total treatment time. The film was characterized with Water Contact Angle (WCA), Fourier Transformed Infrared Attenuated Total Reflectance (FTIR-ATR), X-ray Photoelectron Spectroscopy (XPS) and Atomic Force Microscope (AFM). Thin films deposited at lower power input show high -COOH concentration and hydrophylicity. On the other hand, the strong interaction with water molecules, gave rise to delamination of the coating when the plasma treated substrates were soaked in water and PBS because of the low cross-linked structure of coatings. By increasing the RF power input, a decreased retention of -COOH groups and a lower coating hydrophylicity were observed. Such coatings show high stability in water at room temperature. However, a further increase in RF power input was found to be necessary to obtain high cross-linked coatings, stable also in PBS at 37°C.

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High-Power Pulsed Reactive Magnetron Deposition of TiN Films

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High-power pulsed reactive magnetron deposition of TiN films on Si(100) and steel substrates was investigated. The repetition frequency was in the range from 1 to 20kHz at a fixed 20% duty cycle, a total gas pressure of 1Pa and a substrate temperature of 400°C. Time

evolutions of the discharge characteristics were measured in a 90%Ar+10%N_2 gas mixture at a target power density in a pulse up to 460W/cm^2. Time-averaged mass spectroscopy was performed at a substrate position located 100mm from the target. It was shown that argon ions are strongly dominant (68-85%) in total ion fluxes onto the substrate. With increasing preset average pulse currents at a fixed 10kHz frequency and with increasing frequencies at a fixed average pulse current, the ion energy distributions were more extended to higher energies (up to 50eV relative to ground potential). The increasing ion energies and fluxes, together with the increase in the N^+/N_2^+ ratio, resulted in changes in structure and mechanical properties (hardness up to 27GPa) of the prepared TiN films.

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