Material surface modifications with an inductive plasma

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Abstract. We report on the application of a radiofrequency plasma to surface treatment of materials. Plasma is produced in a low pressure flowing gas by means of an external coil, to prevent direct interaction of the plasma with the radiofrequency electrode. Very stable and steady plasma conditions have been obtained. The plasma state has been characterized by Langmuir probes and optical emission spectroscopy to relate the physical properties of the plasma to the induced surface modifications. The source was applied to perform plasma treatments on a PVC film, in order to obtain a conductive surface layer. We report a preferential removal of chlorine and a superficial generation of C=C double bonds. Imaging of the surface with a FIB/SEM microscope revealed the partial conductivity of the sample and the presence of bidimensional clusters with average radius of about 200 nm.

1. Introduction and experimental setup

The research on low pressure discharges is of great interest because of its applications, in particular for the treatment of polymeric materials [1, 2]. Depending on the gas mixture used for the plasma production different processes like film deposition, etching, polymerisation and activation can be performed to modify the material surface. The present research concerns the characterization of plasma produced by a radiofrequency (RF) discharge inside a vacuum chamber in a low pressure gas-flow. Plasma etching removes preferentially chlorine and hydrogen from the surface [3, 4]. Dehydrochlorination will result in the formation of polyene. As suggested long time ago, conjugated C=C bonds could make the polymer surface conductive [5]. Plasma reactor is built around a pyrex cylinder (length:20 cm, diameter:10 cm) evacuated by a two-stage rotary pump (limit pressure 0.3 Pa). A Pirani gauge monitors the pressure during discharges performed in a gas flowing along the axis of the cylinder and controlled by a micrometer leak valve. Pressure ranges from 10 to 100 Pa, in argon and nitrogen, where stable plasmas can be obtained and maintained for many tens of minutes. Discharge is ignited and fed by a 13.56 MHz RF supply, coupled to the vacuum tube by means of an externally wrapped coil (length:10 cm, turns:15) through a matching network. In this way we have a λ/4 antenna configuration [6] which can sustain discharges with low powers down to 5 W. A fan coil allows to dissipate heat which allows steady operating conditions up to 300 W power. RF dispersion outside the chamber is limited by a metallic grounded shield surrounding the reactor. A layout...
of the setup is displayed in fig.1. Materials to be treated are fixed to a copper ring located in the tube perpendicular to the gas flow.

2. Plasma diagnostics

In order to get quantitative informations about the plasma, a RF-shielded Langmuir probe was used [7]. A resonant filter was embedded into probe body, resulting in a very high impedance at 13.56 MHz. This allows to measure the Langmuir characteristics also in a large RF power environment [8]. The probe can be inserted and moved inside the vacuum chamber. The floating potential and the ion saturation current were recorded in different points of the cylinder axis under different operating conditions regard to power and pressure. We applied optical emission spectroscopy (OES) to extract information about the discharge gas-phase. We used a low resolution, wide band calibrated spectrometer (PS2000 by Ocean Optics) equipped with a 10 µm slit and a holographic grating (600 lines/mm, blazed at 400 nm). The discharge was observed with an UV enhanced optical fiber mounted on a vacuum feedthrough looking along the axis of the cylinder. Atomic emission lines from argon are easily detected and their relative intensity can be measured in different operating conditions. To extract the mean electron temperature we applied a method recently suggested by Mariotti et al. [9], based on a simplified radiative model of the discharge spectra. It exploits the different electron temperature dependence of the cross section of a few excited levels emitting in the visible [10]. Differences in the emission line relative intensity reflect changes in the population of the excited levels which depend on the electron temperature and possibly on metastables concentration. In our application we use intensities of nine emission lines, each corresponding to a different excited 4p argon level to define a sort of \( \chi^2 \) function:

\[
\chi^2 = \sum_{n=1,9} \left[ \left( \frac{R_n}{R_{n+1}} - 1 \right)^2 + \left( \frac{R_{n+1}}{R_n} - 1 \right)^2 \right] + \left( \frac{I_n}{b_n} - \frac{k_n(T_e)}{k_n(T_e)} \right) \cdot (1 - \sum x^{(s)}) + \sum k^{(s)}(T_e) \cdot x^{(s)}
\]

where \( I \) is the measured intensity of the selected emission line and \( b \) is the branching ratio of that transition from the selected excited level. Then \( k \) and \( k^{(s)} \) are the electron impact transition rate to the \( n \)-th excited level, respectively from the ground state and from the two metastable states, and \( x^{(s)} \) are the metastable concentrations. Minimization of the \( \chi^2 \) function respect to the parameters \( (T_e \) and \( x^{(s)} \) allows to extract the electron temperature. Our data do not allow to extract significant information on metastable concentrations but only some upper limit at \( 10^{-4} \) level. In our view, this procedure is more sensible, reducing the systematic errors which could affect the proposed analytical solution [9]. Fair reproduction of the nine
measured intensities, within a factor two, is generally obtained, with $\chi^2/18 \sim 1$. Results from the characterization of the plasma state are displayed in fig.2, 3 and 4. Electron temperatures are almost independent on the power level, which strongly affects the plasma density and the emission intensity. It decreases steadily as the pressure rises, with values in the range 1-1.5 eV. Plasma density reaches values about $10^9$ cm$^{-3}$ and peaks approximately at the position of the high voltage side of the coil. Density increases smoothly with RF power. In the higher side of the pressure range plasma density rises proportional to the square root of power and appears to saturate at large powers. At lower pressures the increase becomes linear. At a fixed power level the plasma density peaks at a pressure of 60 Pa. Static, i.e. DC, positive plasma potentials have been measured, with large values around 50 V. This corresponds to static radial electric fields of about $10^3$ V/m. Along the cylinder axis the potential increases towards the position corresponding to the grounded side of the coil. OES reveals mostly emission lines from neutral argon, with a few lines from impurities, mainly hydrogen, nitrogen and carbon oxide. Most intense lines come from emission of electrons excited in the 4p energy levels. A few lines emitted from electrons in the 4d, 5p and 6s levels have been detected with very small intensity, less than 5% of the brightest ones. This confirms the relative importance of highly excited energy levels, neglected in the approximated radiative model used in ref. [9]. All the nine emission lines considered in the model show a similar trend respect to the pressure and the RF power level. Line intensity increases almost linearly with the RF power. Most of the lines display a peak in intensity at the pressure of 60 Pa.

3. Plasma processing

The source was applied to perform plasma etching onto PVC films. The aim was to remove the hydrogen and chlorine and to enrich the surface with C=C double bonds. Good results have been obtained with argon plasma treatment at 30 Pa pressure and 100 W RF power lasting about six hours. XPS analysis revealed the large decrease in the chlorine content from about 10% to about 1%, with an increase of the carbon content from about 75% to more than 85%. On the other hand, XPS analysis reveals an increase in the oxygen and nitrogen content (from 9.5% to 11.3% and from 0.6% to 2.2% respectively), probably due to air contamination in the plasma chamber or to post-exposure reactions of the treated sample with air. ATR analysis (see fig.5) confirms the C=C double bonds formation (peak at 1637 cm$^{-1}$) and the insertion of
oxygen-containing species on the surface of treated samples (peaks at 1718 cm$^{-1}$ and 3100-3600 cm$^{-1}$). The presence of conjugated C=C bonds could be possibly related to the UV/Vis/NIR transmission spectra, since we found that the film, initially transparent, becomes deep brown after the treatment, with strong adsorption below 700 nm, as already reported in literature [3]. Observation of the sample with a dual FIB/SEM microscope was performed too. While untreated PVC cannot be scanned, because of the charging due to poor conductivity, images of the treated samples have been obtained. This indicates that partial surface conductivity has been obtained. A dedicated diagnostics is then needed to fully characterize the value and limits of plasma induced conductivity. Surface details can be imaged with the ion beam, as shown in fig.6. This reveals clearly the presence of structures with enhanced luminosity forming clusters with average radius of about 200 nm.

4. Conclusions

The characterization of a radiofrequency plasma source used to treat surfaces of plastic materials was presented. Very stable and steady plasma state can be maintained for a few hours in an argon flow. Plasma parameters have been measured as a function of the RF power and of the argon pressure. Electron temperatures are found to be around 1 eV, while plasma density reaches $10^9$ cm$^{-3}$. Application of the source to the treatment of PVC results in the selective removal of hydrogen and chlorine from the surface and in an increase of the C=C bonds which leads to a partial surface conductivity, with the formation of a pattern of clusters with sizes around hundred nanometers.

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