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MATERIALS PROCESSING WITH RADIOFREQUENCY PLASMAS AT LOW AND ATMOSPHERIC PRESSURE

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Abstract. The paper presents a few examples relevant for the application of radiofrequency plasmas for processing of materials and surfaces. The examples have been chosen in order to match the trends in plasma processing science, namely processing at atmospheric pressure, growth of nanostructured materials and design of filtration systems responsive to external stimuli.

Key words: plasma processing, radiofrequency plasmas, nanostructured carbon, plasma sources, plasma treatment of polymers, track membranes.

1. INTRODUCTION

Plasma is one of the tools that can improve existing materials or create new materials. The plasma particles carry out at surface kinetic, electrical, chemical energy, producing material modification, specifically deposition (particles condensate or form stable compounds), erosion (particles sputter or form volatile compounds), or functionalization (radicals bound at surface). The material is modified by the mean of atomistic particles, so plasma processing science has strong significance for the modern technologies. The actual challenges are related to engineering, nanotechnology, biology, as example: i) casting thin films and features with functional properties similar to traditional bulk materials (piezo-, ferro-, dielectric, optic, magnetic); ii) creating surfaces interacting only with selected molecules or biological entities; iii) making ultra-hydrophilic or ultra-hydrophobic surfaces; iv) synthesizing functional materials structured as nanopowders, nanotubes, nanowalls, quantum dots, superlattices. There are numerous ways to use plasmas for material processing. Plasmas generated by radiofrequency electrical fields have same peculiar advantages in processing: i) at low pressure they have the tendency

to occupy large volumes, so to extend and fill quite uniformly the entire processing space; ii) the coupling of the RF power to the discharge can be performed from outside of the processing chamber (discharges with external electrodes); iii) in some applications, as example thin film deposition by magnetron sputtering, the using of radiofrequency plasmas allows the processing of dielectric materials; v) recently, radiofrequency plasma sources operating at atmospheric pressure have been developed.

In this paper a number of approaches, coming from various material processing topics, will be described and discussed. Specifically, the following approaches will be presented: 1) Jet type plasma sources for surface processing at atmospheric pressure; 2) Carbon material synthesis at low pressure by Radiofrequency Plasma Beam Enhanced Chemical Vapor Deposition with emphasis on nanostructured carbon (nanotubes, nanowalls); 3) Radiofrequency plasma processing of polymers with emphasis on nuclear track membranes modification aiming to obtain "smart membranes".

2. JET TYPE RADIOFREQUENCY PLASMA SOURCES FOR PROCESSING AT ATMOSPHERIC PRESSURE

Low pressure plasma processing of materials is largely used, particularly for thin film deposition in optics and electronics, protective coatings, and surface modification for improving adhesion. Expensive and difficult to handle vacuum equipment is necessary for these applications. Coating, surface treatment and functionalization, sterilization with plasma systems that do not require vacuum are presently approaches of top interest, opening perspectives for low cost technologies and materials. The developing of plasma sources able to work at atmospheric pressure and suitable for material processing is also a scientific challenge. In such applications the respective atmospheric plasma source should produce uniform, large area plasmas or, alternatively, movable plasmas for scanning procedures. In addition, in most cases cold plasmas for processing temperature sensitive substrates are requested. Nevertheless, such requirements are difficult to be fulfilled: the intrinsic nature of plasma phenomena leads to plasma constriction with the pressure increasing and in the same time to temperature increasing by collision induced thermalization. In this paper we will present our particular approach by which cold plasma jets, suitable for modifying surfaces by scanning procedures, can be created at atmospheric pressure.

2.1. THE DISCHARGE CONFIGURATION

The plasma source is based on a capacitively coupled configuration consisting of a small discharge room containing two parallel plate electrodes with low

interelectrodic space (2–10 mm) and a hole in the grounded plate, playing role of nozzle (Fig. 1). The plasma source is powered by a 13.56 MHz radio-frequency generator. It can be mounted on a vacuum chamber. At low pressure (10^{-2} to 1 mbar), in absence of the gas flow, the plasma fills the interelectrodic space. If the sheath thickness is smaller then the hole radius plasma extends through the nozzle outside the discharge room [1].

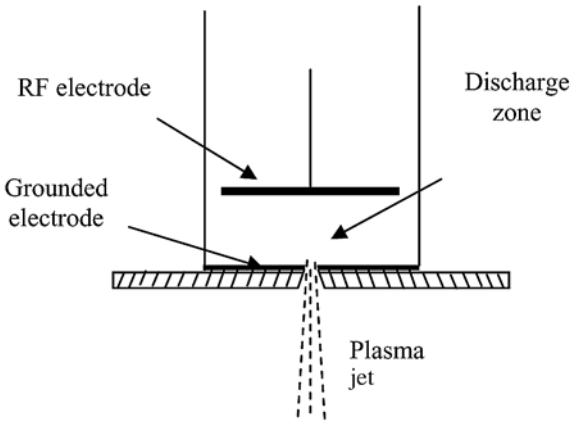


Fig. 1 – Schematic view of the electrodic configuration.

2.2. PLASMA BEAM FORMATION

In presence of a gas flow, the convective effects leads to a long, axisymmetric plasma beam extending outside of the interelectrodic space. At low pressure this plasma beam originates in the volumic discharge generated in the discharge space. Going to atmospheric pressure the plasma in the interelectrodic space becomes constricted due to thermal instabilities [2] and a thin (1–2 mm diameter) plasma column builds-up in between the electrodes. This column is usual unstable and moves around. In the same time the nonequilibrium character changes due to the increased importance of the collisions. The column tends to become hot, and if the cooling is not active enough, the transition to arc will occur. The plasma beam still can be observed, but originates in the columnar discharge and appears to be instable. In the applications foreseen here stable, cold plasmas are necessary. In our approach this is obtained by choosing appropriate mass flow rates and discharge geometries. The gas flow has a cooling effect and stabilizes the constricted plasma on the nozzle exit. This allows decreasing of the RF injected power, so keeping a stable discharge in operation at values that the arc transition is prevented. The presented approach leads to cold plasma generation at atmospheric pressure. Atmospheric plasma sources based on this approach can be designed to have small size and are compatible with scanning procedures. A source built-up on this principle is shown in Fig. 2. This produces a plasma jet of around 0.5 mm diameter, which in argon has a 5–10 mm length.

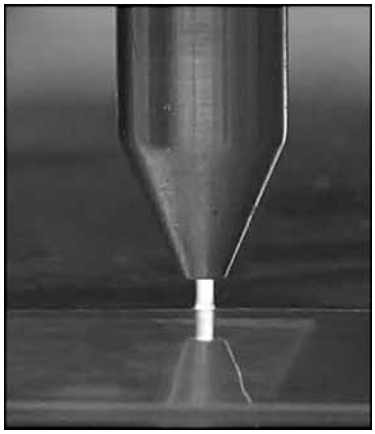


Fig. 2 – Imagine of a small size plasma source (the outer diameter of the source is 8 mm).

2.3. SURFACE MODIFICATION AT ATMOSPHERIC PRESSURE

The thermal loading of the plasmagen gas is low, as shown in Fig. 3 where the dependence of the temperature measured by a thermocouple inserted in the plasma jet upon the forwarded power is shown. Consequently, the heating of the processed surfaces is low. This allows surface modification, without thermal degradation, of polymers. Polymers are known for their low wetability, making difficult their dyeing and printing. The contact angle of untreated polyethylene terephtalate (PET) surface is around 85 degrees. In Fig. 4 is presented the evolution of contact angle upon treatment time (equivalent of a number of scans) with the plasma jet generated in argon. After only 1 second (5 scans, scanning speed 5 mm/s) of the surface the contact angle decreases to less than 50 degrees. This effect is related to the incorporation at surface of polar chemical groups, created in plasma by mixing of argon with oxygen, nitrogen and water vapour impurities from the atmosphere.

One of the most important potential applications of such small size, low power, atmospheric pressure plasma sources could be the patterning of polymeric surfaces

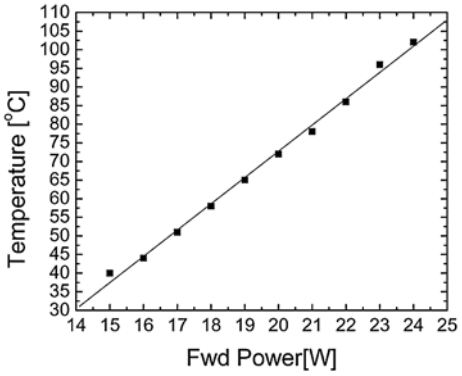


Fig. 3 – The dependence of the temperature in the plasma beam upon power.

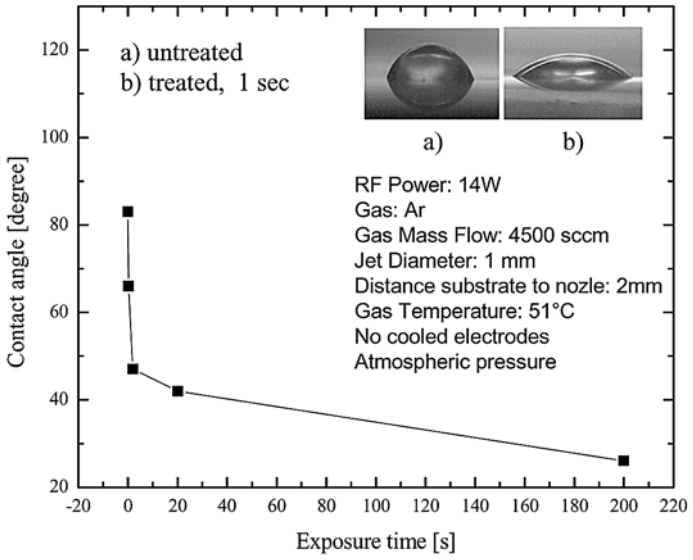


Fig. 4 – Evolution of the contact angle with the treatment time. Inset are presented images of a water drop on the untreated and treated surfaces.

with wettable traces, with sizes in the range of hundreds of microns. Another application of atmospheric plasma source jets presented before is the cleaning of carbon from surfaces, as example for the removal of tritiated co-deposited layers on the Tokamak tiles [3].

3. NANOSTRUCTURED CARBON DEPOSITION AT LOW PRESSURE BY RADIOFREQUENCY PLASMA BEAM ENHANCED CHEMICAL VAPOR DEPOSITION

Carbon can be considered as unique element due to its capability to give complex structures unfounded to other element. Many methods [4] as thermal and plasma CVD, arc discharge, magnetron sputtering, laser ablation were used for deposition of synthetic carbon materials and carbon based material. Carbon materials have a long history in plasma processing, starting with carbonaceous films, plasma polymers, and diamond like carbon (DLC) and continuing with the new nanostructured materials (fullerenes, carbon nanotubes (CNTs), carbon nanowalls (CNWs)) based on hexagonal networks of carbon atoms.

Previously we reported the successful growth of carbon nitride [5], amorphous hydrogenated carbon [6] or nanostructurated carbon [7–10] in a radiofrequency plasma beam. In this paper we will present aspects regarding the conditions of carbon nanowalls growth.

3.1. EXPERIMENTAL DETAILS

The technique is based again on a radiofrequency plasma beam, this time operated at low pressure. The sketch of the used set-up was presented in detail previously [8, 10]. It consists of a cylindrical deposition reactor on which two plasma sources are mounted. First source is a RF expanding plasma jet, generated as described before (Fig. 1), vertically oriented from the reactor top. The second one is a home made, small size, DC magnetron used for sputtering a metallic target which allows catalyst (in the present case nickel nanoparticles) deposition onto substrate. The substrate holder can be rotated to expose its face to the plasma jet, to the magnetron plasma or to both of them. The carbon deposition experiments are of combined type [11], gathering simultaneously two techniques, in this case the Plasma

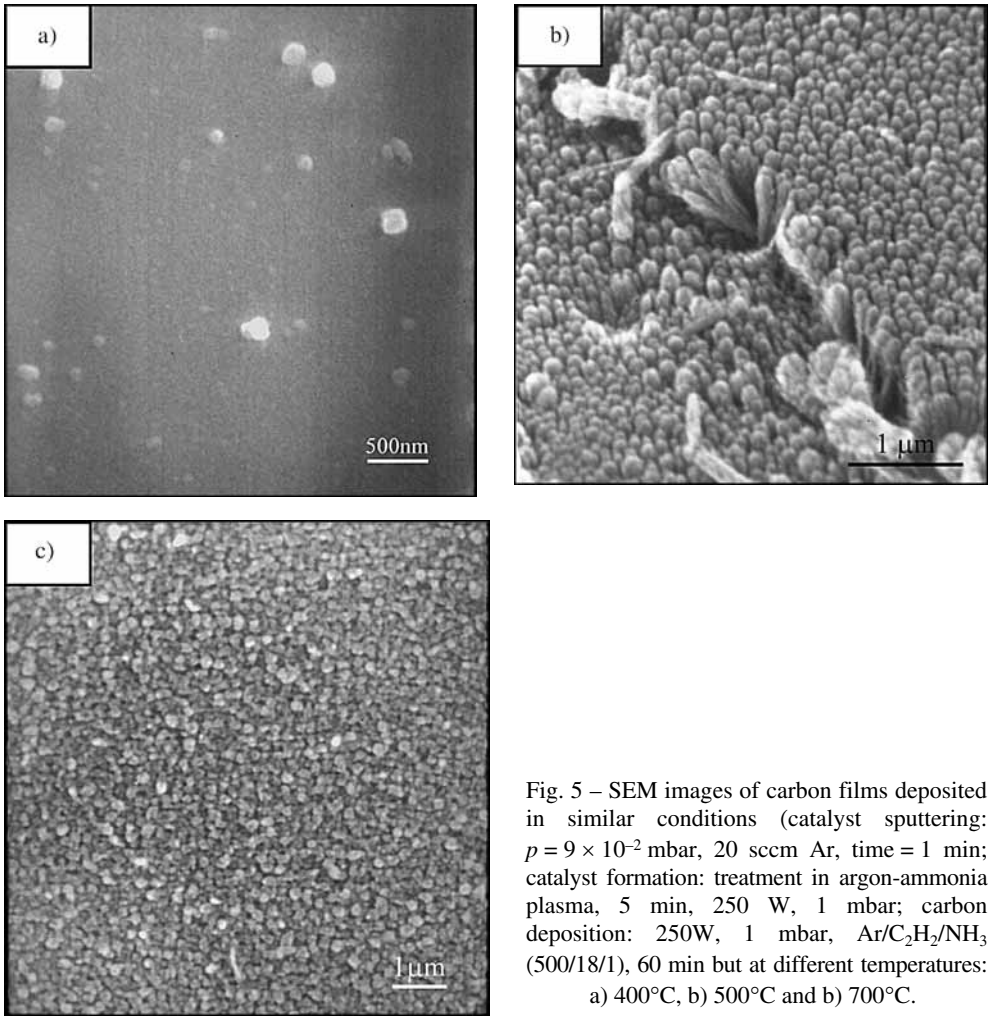


Fig. 5 – SEM images of carbon films deposited in similar conditions (catalyst sputtering: $p = 9 \times 10^{-2}$ mbar, 20 sccm Ar, time = 1 min; catalyst formation: treatment in argon-ammonia plasma, 5 min, 250 W, 1 mbar; carbon deposition: 250W, 1 mbar, $Ar/C_2H_2/NH_3$ (500/18/1), 60 min but at different temperatures: a) 400°C, b) 500°C and b) 700°C.

Enhanced Chemical Vapor Deposition (PECVD) for the growth of carbon material, and the magnetron sputtering (MS) for the catalytic activation of the substrate.

3.2. GROWTH OF NANOSTRUCTURED CARBON

Details on the processes responsible for carbon nanowalls deposition have been presented elsewhere [10], including a discussion about the mechanism of combined growth of nanotubes and nanowalls [9]. The growth is based on the carbon radicals produced by dissociation of acetylene precursor injected in argon plasma jet, in presence of an active gas, like ammonia or hydrogen. The radicals are transported by the plasma flow at a substrate positioned downstream the generation zone. The growth is stimulated by the presence of nickel nanoparticles.

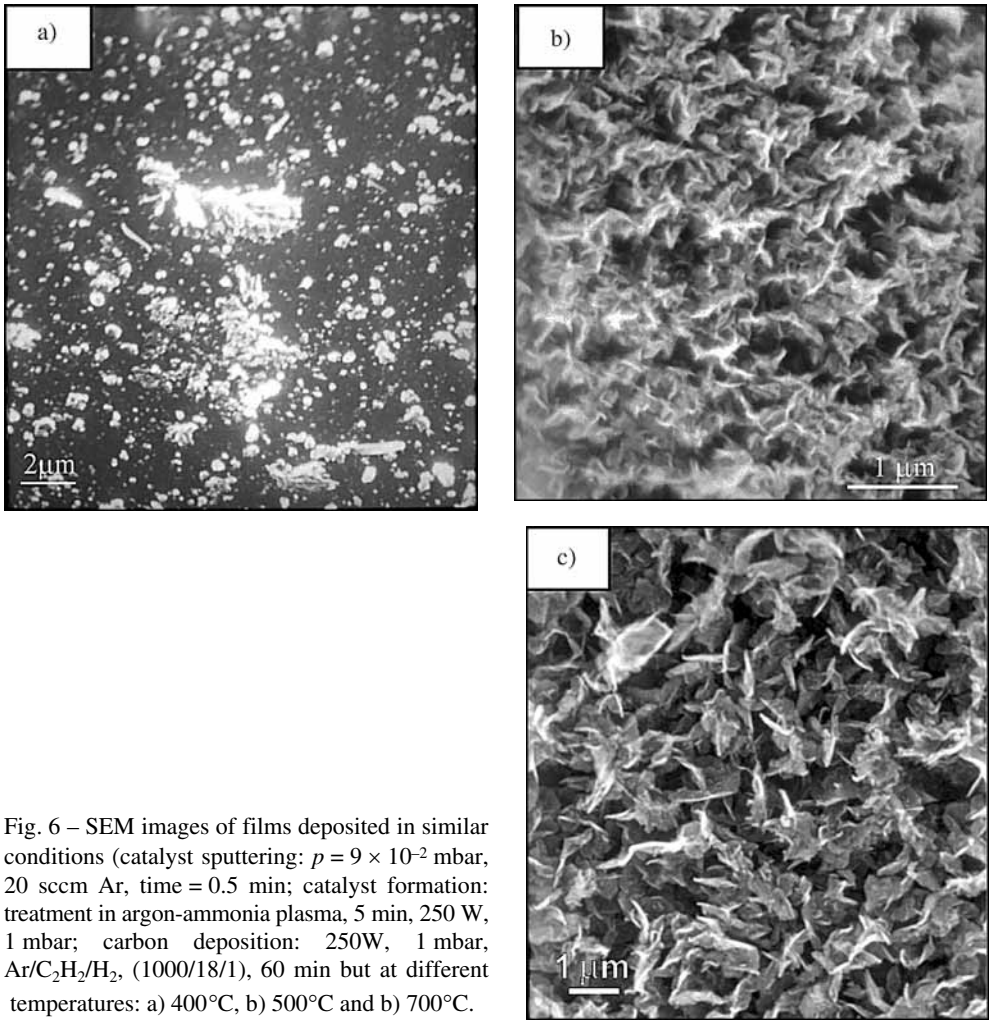


Fig. 6 – SEM images of films deposited in similar conditions (catalyst sputtering: $p = 9 \times 10^{-2}$ mbar, 20 sccm Ar, time = 0.5 min; catalyst formation: treatment in argon-ammonia plasma, 5 min, 250 W, 1 mbar; carbon deposition: 250W, 1 mbar, $Ar/C_2H_2/H_2$, (1000/18/1), 60 min but at different temperatures: a) 400°C, b) 500°C and b) 700°C.

The temperature of substrate and the nature of active gas (ammonia or hydrogen) are parameters which influence drastically the morphology of the obtained material. This is described below by SEM investigations of samples resulted from two series of experiments.

In a first series of experiments ammonia was used as active gas, and deposition was performed at 400°C, 500°C and 700°C. While at 400°C the material is only slightly nanostructured, going to higher temperature acicular carbon nanostructures (carbon nanofibers) are formed (Fig. 5).

In a second series of experiments hydrogen was used as active gas. The morphology of the obtained material is presented in Fig. 6. The increase of the temperature helps the nanostructures formation, but this time carbon nanowalls are formed at high temperature.

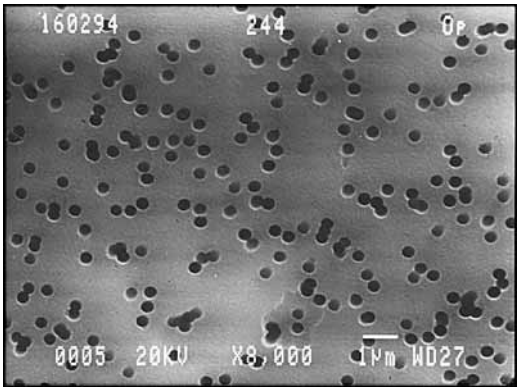
However, the exact reason leading to nanowalls growth in case of hydrogen containing plasma is difficult to be established. It is thought that the concentration of radicals at substrate plays the most important role, as has been suggested recently [12]. A more detailed study based on Optical Emission Spectroscopy indicates in case of nanowalls growth a prominent emission of the C_2 radical at the substrate proximity [10].

4. RADIOFREQUENCY PLASMA PROCESSING OF NUCLEAR TRACK MEMBRANES

Polymeric membranes have a wide range of applications in various domains, like biology, chemistry, pharmaceutical and food industry. Particularly, the nuclear track membranes are useful because of their narrow pore distribution. They are obtained by irradiation of thin polymeric foils with high energy (a few MeV/nucleon) heavy ions. The material is damaged along the pore trajectories and is removed in a later step by chemical attack with caustic solution. The result is a polymeric foil with pores of almost equal diameter, randomly distributed on the surface (Fig. 7).

The plasma treatment is an effective method for modifying the pore size and shape, by etching the polymeric surface [13] As well, by surface activation the hydrophobic character can be changed to a hydrophilic one. By plasma polymerization of a monomer introduced in the discharge an additional layer can be grown on the surface. This layer can be further developed by a polymerization reaction leading to grafting of monomer molecules on the surface.

Nowadays there is an increased interest in making “smart” systems which regulate themselves in accord with the presence or the intensity of external stimuli. An approach which can lead to “smart” track membranes that can work as filtration valves is presented in this section of the paper. The approach is based on the building up at the membrane surface and partially inside the pores of a thin layer of



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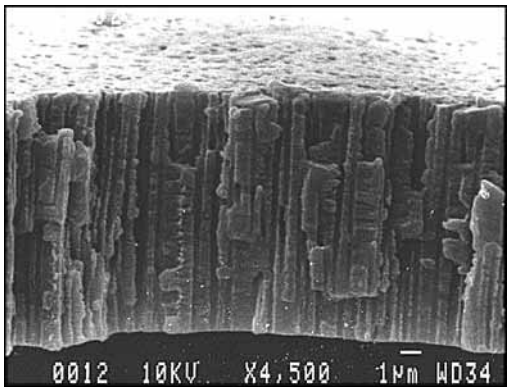


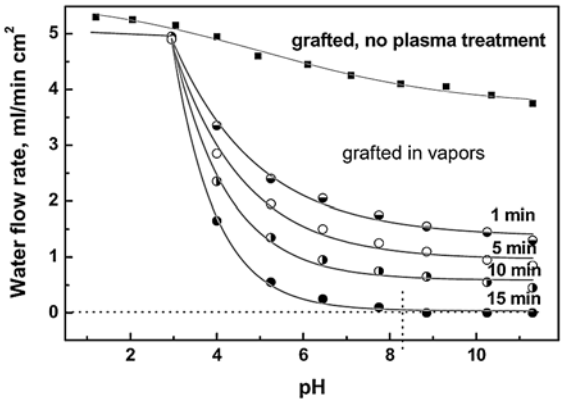
b)

Fig. 7 – Images of nuclear track membranes a) front view, b) profile view.

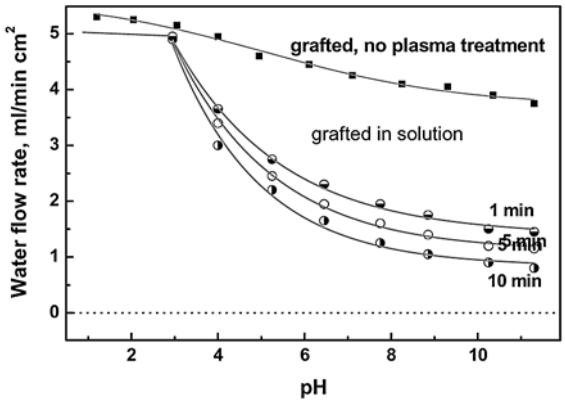
macromolecular material whose volume depends on the external conditions. Particularly, the conformational state of polyacrylic acid molecular chains depends on pH. At low pH values the molecular chains have a closed structure, while at large pH values they have a loose structure. Consequently, a film of polyacrylic acid in water will change its thickness according to the water pH.

In the present experiments plasma was used as tool to deposit a polyacrylic-like thin film on polyethylene terephthalate (PET) track membranes with thickness of 10 μm, pore density of $2 \cdot 10^8$ cm^{-2}, and effective pore diameters of 0.215 μm. Grafting was involved afterward in order to increase the length of molecular chains. The experimental set-up for plasma treatments was presented in detail elsewhere [14] It consists of a plasma polymerization reactor, in which two planar parallel electrodes allows the generation of a radiofrequency discharge (13.56 MHz) in vacuum (10^{-2} – 1 mbar). The RF electrode is designed as a shower and is used for gas and precursor injection. The lower electrode is used as holder for the membrane. The experiments were performed at an RF power of 60 W, pressure at 2×10^{-1} mbar and Ar/acid acrylic vapor flow of 25 sccm.

In a first step, a layer of polymer-like acrylic acid was built-up by plasma polymerization using treatment times in the range 1–15 min. Membrane characteristics changed, proving that the deposition process was effective: the mass and the thickness increased and the pore size decreased with the deposition time. Further on the plasma treated membranes were immersed in vapors of acrylic acid (1 h at 75°C, followed by washing with deionized water for 14 h) or in solution of acrylic acid (conc. 25%, 14 h at RT, followed by washing in deionized water for 9 hours) aiming to graft and increase the length of the incipient molecular chains seeded by plasma.



a)



b)

Fig. 8 – The water flow rate dependence upon pH for: a) plasma polymerized track membranes grafted in acrylic acid vapors, b) plasma polymerized track membranes grafted in solution of acrylic acid.

The water permeability of the hybrid system consisting of the membrane and the deposited/grafted film was used as indicator for flow control as function of pH. In Fig. 8 a and b are presented the dependence of the water flow rate upon pH for the plasma polymerized track membranes grafted in vapors and solution of acrylic acid. It is observed that in both cases the permeability to water decreases with the

pH increase. The most favorable case corresponds to vapor grafting and plasma treated membranes for 15 min (the lowest curve in Fig. 8a). In this case the filtration changes for full rate at pH values less than 3.5 to zero value at pH value larger than 8.5. The explanation for this effect is related to the conformational state of the polyacrylic acid molecules. At low pH the polymerized/ grafted molecules let the pores open and at high pH they close the pores. The curves in Fig. 8 indicate that filtration devices acting as chemical valves can be obtained by plasma polymerization and grafting.

We like to notice that this kind of asymmetric porous systems, consisting of a base porous layer and thin functional plasma deposited film present other interesting properties as well, as example, asymmetric conductivities of the ions present in solutions.

5. CONCLUSIONS

The potential of radiofrequency discharges in material processing is demonstrated by selected study cases. In the case of processing at atmospheric pressure the most important results are related to the design of small size plasma sources which produce cold plasmas. Such sources are promising tools for treatment of temperature sensitive substrates, modification of surface energy of polymeric foils and their patterning with wettable traces. The second example focuses on creation of new materials and shows how plasma can be used to produce carbon nanowalls. The substrate condition and the plasma composition are the key factors which control the material morphology. Finally, it is shown that with plasma is possible to tailor the filtration properties of nuclear track membrane and to create "smart" filtration systems, which self-change their filtration rate upon the solution pH. These examples demonstrate that this area is strongly connected to the recent advances in science and technology and can offer solutions for a large range of problems from engineering, nanotechnology and product design.

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