Plasma-assisted tailoring of fractal architecture of poly(ethylene) nano-islands

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Abstract: Low-temperature plasma methods have a long list of successful applications where are crucial to fabricate surfaces with nano-scale accuracy. Here, fractal nano-islands of poly(ethylene) were grown on silicon using plasma-assisted vapor phase deposition. The island shapes were characterized in a framework of fractal analysis, which offers feasible approach to describe morphology numerically.

Keywords: poly(ethylene), RF plasma, island growth, dendrite, fractal dimension

1. Introduction
Nano-structured polymeric thin films provide a unique platform for development and realization of diverse applications. Production of surface patterns with desired properties (e.g. size and shape, chemical composition etc.) can be implemented by depositing thin films onto solid substrates. Over the last decades, a number of techniques were developed to enable the production of nano-structured polymeric surfaces. These include glow discharge-based methods employed for fabrication of plasma polymers [1]. Although plasma polymers are commonly produced in a form of smooth and homogeneous coatings, there is increasing interest in production of nano-structured plasma polymerized coatings and in investigation of their formation in the early stages of film growth. Recently, De Vriendt et al. demonstrated dendritic submonolayer film of plasma polymer obtained by pulsed plasma polymerization of acetylene [2].

The purpose of this study is to introduce plasma-assisted vapor phase deposition of poly(ethylene) (PE) for fabrication of polymeric nano-patterns and to demonstrate the capabilities of this method for adjusting the surface nano-architecture. Fractal analysis is applied to specimens as a quantitative method for characterizing complex irregular structures.

2. Experimental
A schematic diagram of the experimental set-up for the production of nano-structured thin films is shown in Fig. 1. The experiments were performed in a cylindrical vacuum chamber of 0.04 m³ volume pumped with rotary and diffusion pumps to a base pressure of 4×10⁻⁴ Pa. After reaching the base pressure, argon was let into the chamber at a 5 sccm flow rate and the working pressure was set at 1 Pa. PE granules (Sigma-Aldrich) were loaded into a copper crucible, which rested on two molybdenum stripes heated by electric current. The crucible with polymer was placed 4 cm above a r.f. magnetron (Dressler Ceasar, 13.56 MHz). The magnetron with a graphite target was used to ignite glow discharge when required. Polished silicon wafers were used as the substrates. The substrates were placed 24 cm above the magnetron. A quartz crystal microbalance (QCM) was placed 14 cm above the magnetron to maintain the constant deposition rate (20 Hz/min). During a pre-adjustment stage, the substrates were residing in a load-lock chamber and after stabilization of the deposition conditions they were introduced to their working position above the crucible. For obtaining coatings with different morphology, all the experimental parameters (Ar pressure and flow rate, PE evaporation rate, deposition time) were fixed except for the magnetron power. The deposition time was set to 30 minutes. To produce compact islands vapor phase deposition (VPD) was performed without plasma ignition. Dendrite plasma polymers were fabricated by simultaneous VPD of PE and activation of the evaporated flux with a glow discharge at a delivered power to the magnetron of 5 W.

Fig. 1. Schematics of the experimental set-up. C – copper crucible loaded with granules of PE, QCM – quartz crystal microbalance, M – water cooled planar RF magnetron, T – circular graphite target, Sh – shutter, S – silicon substrates on substrate holder.
Atomic Force Microscope (Ntegra Prima, NT-MDT) has been used in a semi-contact mode under ambient conditions to characterize the resulting film morphology ex-situ.

Gel permeation chromatography (PL-GPC 220 with PL-220DRI refractive index detector, columns 3x PL gel 10 μm MIXED-B, 300 x 7.5 mm, with guard column PL gel 10 μm MIXED-B, 50 x 7.5 mm) was used to establish the molar mass distribution of the resultant polymeric deposits as well as of the precursor PE. The sample solutions were prepared in filtered 1,2,4-trichlorobenzene for chromatography (Scharlau) containing 0.025 wt% of an antioxidant Santonox R to prevent oxidative degradation of polymers. The GPC analysis was performed at 160 °C. For calibration, poly(styrene) standards were used (Waters a Polymer Laboratories).

3. Results and discussion
The research of activation of PE volatile fragments in a r.f. glow discharges was started by our group [3]. Vacuum thermal decomposition of PE with or without ignited plasma was employed for the deposition of thin films. The released organic vapors become fragmented and with significant presence of free radicals as a result of the passage of evaporated species through a glow discharge. According to [3] plasma activation of PE enhanced crosslinking of the resultant film but at moderate powers prepared samples resemble the original PE precursor used for evaporation.

![Fig. 2. Molar mass distribution of the PE precursor, the film prepared by vapor phase deposition of PE on Si and the film prepared by plasma-assisted vapor phase deposition of PE over Si (delivered power - 5 W) as determined by GPC.](image)

A complement view on the chemical composition is given by GPC measurements analysed in terms of average molar mass and dispersity. Molar mass distributions are depicted in Fig. 2. A flux of the low mass oligomer generated by thermal degradation of PE precursor (M<sub>n</sub> = 19355 g/mol, D = 9.36) produces film with narrow and symmetric molar mass distribution (M<sub>n</sub> = 1384 g/mol, D = 1.10). In contrast, plasma assisted deposit represents a highly cross-linked and irregular macromolecular network (M<sub>n</sub> = 4807 g/mol, D = 19.18) as a consequence of randomness of plasma polymerization process.

![Fig. 3. 50×50 μm<sup>2</sup> AFM height images with 16 nm z-scale of (a) PE film on Si fabricated by vapor phase deposition and (b) PE-like plasma polymer film on Si prepared by plasma-assisted evaporation. (c) 2×2 μm<sup>2</sup> AFM image of a single island. (d) 5×5 μm<sup>2</sup> AFM image of a single dendrite. (e), (f) Corresponding cross-sections indicated by the blue line in (c) and (d).](image)

Fundamental understanding of the organic film growth mechanisms can only be achieved by investigating the initial stages of first layer growth. The AFM analysis in Fig. 3 demonstrates the typical morphology of PE film prepared without (a, c) and with (b, d) the assisting plasma at the early stages of the deposition onto atomically smooth Si substrates. Clearly, the glow discharge influenced significantly the island shape. The film fabricated by vapor phase deposition consists of compact two-dimensional (2D) islands of 7-8 nm thickness (Fig. 3e). With the plasma turned on, the deposited material self-organizes into the dendritic nanostructures with the island height of 6-7 nm (Fig. 3f).

We demonstrated recently that attachment barrier and relaxation of the macromolecular chains along the island edge cause compact shape of the PE islands [4]. In the case of plasma deposition, the shape of islands transforms from compact to dendritic. Being extremely reactive, free radicals acts as cross-linkers when they arrive with a flux...
of oligomers at the substrate and take part in recombination reactions. Limited mobility of macromolecular segments, which is connected with recombination of radicals and formation of covalent bonds, increases a probability of irreversible sticking between diffusing particles and islands. This in turn leads to formation of nano-islands with highly dendritic character.

Fig. 4. Fractal dimension determination by the box-counting method of the structures fabricated with and without plasma assistance.

The existence of diverse island shapes needs a morphological technique to quantify and characterize PE nano-structures. To assess a complexity of the island morphology, we determined their fractal dimension by the box-counting method using the ImageJ shareware program from NIH laboratory (Fig. 4). The software was tested on the structures of known fractal dimension and gave accuracy within a few percent [5]. The average fractal dimension for the compact islands formed without plasma was 1.92±0.02. The fractal dimension obtained for plasma-processed dendritic islands was 1.71±0.03. These results quantitatively confirm that the dendritic type of the islands has a highly ramified structure.

4. Conclusions
   Plasma-assisted physical vapour deposition of PE onto silicon fabricates dendrite aggregates at initial stages of deposition. The morphology of the aggregates has been confirmed to be fractal by the box-counting determination method. This scanty category of nano-structured plasma polymers can reveal new insights of kinetics of macromolecules at solid/vacuum interface.
   Future studies will be dedicated to the understanding the processes underlying the growth of ultrathin dendritic films in dependence on the process parameters and to the detailed quantification of different morphologies by fractal analysis.

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6. References