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Polymer deposition morphology by electrospray deposition - Modifications through distance variation

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ABSTRACT

Electrospray deposition (ESD) of highly diluted polymers was examined with regard to the deposited surface structure. Only the flight distance (flight time) onto the resulting deposited surface was varied from 20 to 200 mm.

An apparatus without any additional heating or gas flows was used. Polyacrylic acid (PAA) and polyallylamine (PAAm) in methanol were deposited on Si wafers. The polymer layers were characterized by scanning electron microscopy, X-ray photoelectron spectroscopy, derivatization reactions and Fourier transform infrared spectroscopy using a grazing incidence unit.

SEM images illustrated the changing structures of PAA and PAAm. For PAA the deposited structure changed from a smooth film (20 mm) to a film with individual droplets on the coated surface (100 mm and 200 mm), while for PAAm individual droplets can be seen at all distances. The ESD process with cascades of splitting droplets slows down for PAA after distances greater than 40 mm. In contrast, the ESD process for PAAm is nearly stopped within the first flight distance of 20 mm. Residual solvent analysis showed that most of the solvent evaporated within the first 20 mm capillary-sample distance.

1. Introduction

Electrospray deposition (ESD) is a method to transfer macromolecules into the gas phase at atmospheric pressure without fragmentation [1]. Injection of a polymeric solution in a high electrical field leads to an aerosol of charged species (solvent and macromolecules), which can be deposited on the substrate. The sprayed droplets are charged, which simplifies the control of droplet motion and increases the efficiency of deposition on the substrate [2].

The ESD method has some key advantages. The spray process is cheap. The technical equipment required is simple. The process is flexible due to low material consumption and use of atmospheric pressure conditions. A broad variety of ionic and polar polymers can be sprayed.

Hence, ESD promises a wide range of possible applications in industry and research. Plenty of research was done in e.g. inorganic thin film deposition [3–5], encapsulation [6] and biotechnology [7,8]. For further interest in inorganic layer deposition read the review articles of Anatol Jaworek published in 2007 and 2008 [2,9,10].

Another application is pursued by Rietveld in deposition of relatively inert layers with ferroelectricity as feature by poly (vinylidene fluoride) layers [3,11,12]. Less research is done in polymer depositions, which offers the opportunity of functionalization of polyolefins for better adhesion [13].

Our particular interest is focused on thin film deposition and its structure for surface functionalization with chemically interesting functional groups, e. g. COOH and NH_2. The goal is to deposit ultra-thin polymer layers with thickness of less than 10 nm. We presented in earlier work how such films adhere strongly to a number of different substrates [11].

Electrospray depositions in the literature are often denoted with short distances (0–40 mm) [14,15], although the residue amount of solvent on the substrate is a key parameter for film morphology. Therefore, special attention is paid to the evaporation of solvent as a function of the capillary-sample distance.

2. Experimental

2.1. Materials

Polyacrylic acid (PAA, M_w = 450,000 g/mol, Aldrich) and polyallylamine (PAAm, M_w = 65,000 g/mol, Aldrich) were used for ESD deposition. PAAm was supplied as 20 wt.% aqueous solution and PAA as powder. Acetone, ethanol, methanol (0.003% H_2O), pyridine and diethylether were purchased from Merck at purity suitable for analysis. B-doped Si wafers (0.1–20 Ω cm contact resistance) were used as substrate (CrysTech, Berlin).

Derivatization reactions of COOH and NH_2 groups were done with 2,2,2-trifluoroethanol (99.7%, Merck), N,N-di-tert-butylcarbodiimide (>99.0%, Fluka) and 2,3,4,5,6-pentafluorobenzaldehyde (98%, Aldrich).

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For measurements of residual solvent, methanol D4 (99.8%, Merck) was used. Au sputtered Si wafers were used for IRRAS measurements (infrared reflection absorption spectroscopy). Sputtering was performed using an Au sputtering target with a purity of 99.9% in an Edwards Auto 306 Turbo apparatus.

2.2. Technical details of the ESD process

All ESD experiments were done with an in-house constructed electrospray apparatus which is connected to a syringe pump (B. Braun Perfusor secura ft) to supply the polymer solution. The capillary used had a length of 100 mm, an outer diameter of 1.6 mm and an inner diameter of 0.25 mm. The tip of the capillary was sharpened by an angle of 20° to reduce the outer diameter to 0.5 mm for increasing local field strength.

For ESD process, a diluted solution is sprayed out of a charged capillary. The first monodisperse droplets split off into cascades of mother and daughter droplets containing charged solvent and macromolecules. These charged species are guided to the substrate by motion in the electrical field. Theoretical aspects of ESD can be found in previous paper [16].

Solutions of 0.01 wt.% of PAA and PAAm in methanol were freshly prepared for each experiment and homogenized in an ultrasonic bath for 15 min for complete dissolving. Si wafer substrates were cleaned in acetone and ethanol (ultrasonic bath).

ESD layers were deposited with different capillary-sample distances of 20 mm, 40 mm, 100 mm and 200 mm. All experiments were done in cone-jet mode [2] using DC voltage. The capillary operated as an anode, while the substrate was grounded to the mass or to negative potential.

A connection scheme is presented in Fig. 1. Typical currents range from 10 nA to 17 nA.

The amount of deposited material is calculated according to Rietveld by concentration, flow rate and deposition time [3]. The potential between capillary (anode) and sample (cathode) was controlled using two independent voltage sources. Both the electrical current through the capillary and the sample was measured continuously. During the time-of-flight of droplets the influence of disadvantageous potentials from the chamber environment could not be ignored, because additional potential droplets were partially redirected and thus not hitting the substrate. Applying an attractive potential on the sample with equality of cathode and anode current gives a tuning condition were the currents are a measure for the number of charges transported from anode to cathode. Assuming a correlation between the transported electrical charge and solved molecules, we control the amount of material deposition. A nominal layer thickness of an isotropic film with constant thickness is given and was experimentally adjusted to 10 nm.

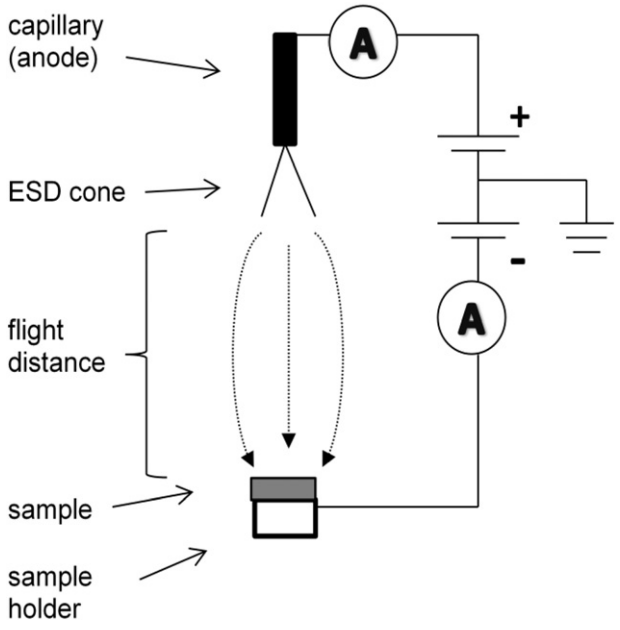

Fig. 1. Scheme for ESI deposition.

The average flow rate was 2 μL/min. The applied potential was chosen between 4 and 8 kV in order to reproduce conditions for cone-jet mode at different capillary-to-substrate distances.

2.3. Analytical characterization

All samples produced were measured by X-ray photoelectron spectroscopy (XPS) using a Sage 150 spectrometer (Specs, Berlin). The angle between the X-ray source and the analyzer is 54.9°. The analyzer is located at an 18° angle to the surface normal. The samples were measured with non-monochromatic AlK_α radiation at a pressure below $3 * 10^{-5}$ Pa.

The measured area is 1×3 mm. The constant analyzer energy mode with 20 eV pass energy is used. Spectra were produced with 18 mA and 11 kV. The peaks were fit to the XPS results using the CasaXPS software package.

Further samples produced under the same conditions were analyzed by scanning electron microscopy (SEM). A Zeiss Gemini Supra 40 microscope was used.

Residual solvent analysis was performed with Au sputtered Si wafers using Fourier transform infrared spectroscopy (FT-IR). The Nexus 8700 spectrometer was equipped with a grazing incidence unit. All spectra were recorded at an angle of 86°.

2.4. Definition: "Coverage"

The coverage ρ of the surface with a deposited layer was determined by XPS as quotient of the atomic content of the deposit to all measured atoms. It represents a weighted averaged surface ratio with coverage thicker than the information depth of XPS.

The XPS spectrum yields the atomic contents of all elements within a surface depth of around 6 nm. Hydrogen is not seen or considered in XPS. A coating ratio of 100% means that a dense layer of at least 6 nm must be present. Thinner layers and partially uncovered areas produce smaller coating ratios, and an uncovered surface results in a coating ratio $\rho = 0\%$.

The atomic content of polymer molecules on the surface must be quantified, but omnipresent hydrocarbon contaminations and other oxygen compounds on metallic or Si substrate surfaces must be excluded from counting.

Here, PAA as a sprayed polymer contributes oxygen and carbon; due to different chemical shifts its C1s signal can be fitted into 5 components (**C**–O and **C**═O, **C**H2, **C**H–COOH and **C**OOH). The significant carbonyl component (COOH), with its shifted binding energy of C1s at about 289.18 eV [17], was chosen to detect and quantify deposited PAA.

Starting from the absolute atomic content of carbonyl group carbon determined, the corresponding carbon content of PAA molecules was calculated by applying the carbon component composition formula established experimentally by Briggs [17]:

$$\text{C-area}(\mathbf{C}\text{OOH}) \,/\, \text{C-area}(\mathbf{C}\text{H2}\mathbf{C}\text{H} - \mathbf{C}\text{OOH}) = 29/100.$$

The stoichiometric formula of the PAA unit defines the corresponding two oxygen atoms per unit and thus the value of PAA atomic content results as:

$$\text{content (PAA)} = 5/3 * \text{content (C of PAA)}.$$

The quotient of the content of PAA and the sum of all atoms at the surface measured by XPS determines the value of coverage sought.