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Erstveröffentlichung in / First published in:
DOI: https://doi.org/10.1117/12.2184807

Diese Version ist verfügbar / This version is available on:
https://nbn-resolving.org/urn:nbn:de:bsz:14-qucosa2-351875

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Dominic Hecker, Daniel Gloess, Peter Frach, Gerald Gerlach, "Electrospray ionization deposition of BSA under vacuum conditions," Proc. SPIE 9517, Smart Sensors, Actuators, and MEMS VII; and Cyber Physical Systems, 951729 (1 June 2015); doi: 10.1117/12.2184807

Event: SPIE Microtechnologies, 2015, Barcelona, Spain
Electrospray ionization deposition of BSA under vacuum conditions

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ABSTRACT

Vacuum deposition techniques like thermal evaporation and CVD with their precise layer control and high layer purity often cannot be applied for the deposition of chemical or biological molecules. The molecules are usually decomposed by heat. To overcome this problem, the Electrospray ionization (ESI) process known from mass spectroscopy is employed to transfer molecules into vacuum and to deposit them on a substrate. In this work, a homemade ESI tool was used to deposit BSA (Bovine serum albumin) layers with high deposition rates. Solutions with different concentrations of BSA were prepared using a methanol:water (MeOH:H2O) mixture (1:1) as solvent. The influence of the substrate distance on the deposition rate and on the transmission current was analyzed. Furthermore, the layer thickness distribution and layer adhesion were investigated.

Keywords: electrospray, ESI, vacuum deposition, BSA, biomolecules, protein

1. INTRODUCTION

Functionalized molecules, biological materials and nano-objects have gained essential importance for sensor applications and electrical devices over the past few years. However, the film produced with commonly used methods such as spin coating or printing are often not pure enough and they lack of thickness uniformity. Vacuum processes, which are used since years in semiconductor and MEMS technology, are a suitable solution to overcome this problem. Unfortunately, conventional vacuum techniques often don’t work for the cited materials, because they have an extremely low vapor pressure. Nevertheless, vacuum deposition is possible using the Electrospray ionization (ESI) process [1,2]. In [1,2], ESI was used to deposit intact biomolecules on a substrate in a UHV chamber using a complex deposition plant. This plant ensures deposition of ultrapure layers but only with a very low deposition rate, due to a quadrupole mass filter. An increase in the deposition rate can be achieved at higher pressures at the cost of a lower film purity.

2. EXPERIMENTAL

ESI principle

During ESI deposition under vacuum conditions, the material is ionized and sprayed through a capillary into the vacuum chamber [1-5] as shown in Figure 1. For that, the usually powdery functional material has to be dissolved previously in a suitable solvent. This solution is pushed through a needle that is on high electrical potential. Because of the difference in the electrical potential of spray needle and capillary, a high electrical field forms and the liquid builds a Taylor cone at the needle tip [6]. From this very small cone, droplets are emerged and accelerated in the direction of the capillary. During transfer into the vacuum, the solvent in the droplets is evaporated and the charge carriers trapped in the droplet get closer together. As soon as the Rayleigh limit is reached, the repulsive forces of the charges are so high that Coulomb explosions take place and the droplets burst into much smaller droplets. This process continues until the whole solvent is evaporated, so that only the organic material without any solvent remains and is deposited onto the substrate.

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ESI setup

The scheme of the ESI deposition tool is shown in Figure 2. The ESI setup is a handmade deposition tool consisting of standard vacuum components (dimensions: 30x30x30 cm), which allows flange-mounting onto commercial vacuum deposition plants. Thus, it enables integration of the ESI deposition into standard vacuum deposition processes. A vacuum pump combination consisting of a rotary vane pump (Balzers DUO 30A) and a mechanical booster pump (Edwards EH500) evacuates the vacuum chamber down to a pressure of approximately 1 mbar. The initial solution is provided by a syringe pump (B.Braun Perfusor Secura FT). The solution is laid on high electrical potential and pushed through a silica tip (New objective, 5 cm length, 100 µm inner diameter) in the direction of the vacuum chamber. The sprayed solution enters the vacuum chamber through a heated (120 °C) stainless steel capillary (0.8 mm diameter, 7 cm length) [1,2]. The substrate is mounted on an adjustable substrate holder located within the chamber. Thus, a substrate bias can be applied and the capillary to substrate distance can be varied. To align the silica tip with the capillary, a xyz-manipulator is used, which allows a precise adjustment of the tip in the sub millimeter range.

Deposition procedure and characterization

Three different initial solutions of BSA (Bovine serum albumin, Aldrich) with the concentration of 2 µM, 20 µM and 200 µM in a 1:1 mixture of methanol (MeOH) and water (H₂O) were prepared. A metal substrate was used for the transmission current measurements and Si wafer pieces were used as substrates for the deposition rate measurements. The deposition parameters are shown in Table 1.
Table 1: Deposition parameters

<table>
<thead>
<tr>
<th>Needle voltage</th>
<th>Chamber pressure</th>
<th>Needle distance</th>
<th>Solvent flow</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 kV</td>
<td>110 Pa</td>
<td>1.5 mm</td>
<td>2 µl/min</td>
</tr>
</tbody>
</table>

The deposition process can be monitored via several measured parameters. This allows evaluation of the reproducibility of the experiments. The decrease of the chamber pressure during the process indicates e.g. an increased coating of the inner surface of the capillary or a potential blockage of the capillary. A decrease of the capillary current can indicate a blockage of the spray needle.

The transmission current measurements were done by the ampere meter of the voltage supply (Iseg SHQ 226L), which was connected to the substrate holder during the experiments. Layer thickness were determined by surface profilometry using the Dektak 150 (Vecco). The SEM investigation was done using the SEM microscope SU8000 (Hitachi).

3. RESULTS

Shape of the coating

A deposited sample is shown in Figure 3. The deposition profile has a circular shape with highest deposition rate at the center. The diameter of the circle depends on the capillary to substrate distance, on the concentration of the initial solution and on the deposition time.

![Figure 3: The picture of the Si substrate shows the deposition area. In the region of the circle is the highest deposition rate. The circle is formed opposite to the capillary. The diameter (here 1.5 cm) depends on the capillary to substrate distance (here 5 cm), on the concentration of the initial solution (here 200 µM) and on the deposition time (here 25 min).](image)

Influence of the distance between capillary and substrate

The influence of the capillary to substrate distance on the deposition rate for solutions with different BSA concentrations is shown in Figure 4. As expected, the deposition rate increases for higher concentrated BSA solutions, because of the higher material supply from the initial solution. For greater capillary to substrate distances, however, the deposition rate decreases. If the distance is too high, the deposition rate even goes down to zero. This effect is probably due to the small mean free path (approx. 10 µm for 100 Pa) and the resulting collisions of BSA molecules with the surrounding gas. Thus, the molecules lose energy and they will be scattered, so that they will be either pumped away or be deposited on the chamber walls.
Figure 4: Dependency of the deposition rate from the substrate to capillary distance

For the transmitted current as a function of the capillary to substrate distance shown in Figure 5, the behaviour is very similar. Here, the transmitted current increases for higher concentrated BSA solutions. This is due to the higher material supply from the initial solution that is charged by the high voltage. The transmitted current decreases with higher capillary to substrate distance. Since the transmitted current is proportional to the amount of charged ions which reach the substrate, it is also an indicator for the deposition rate.

But, at substrate distances where the deposition rate is zero, there is still a significant transmission current measurable. The reason we attribute to collisions of the material with the surrounding gas. During these collisions the material could be also fragmented into much smaller molecules. These fragments contribute to the current, but they contribute almost nothing to the deposition rate. Furthermore, the surrounding gas can be ionized which also could be detected by the amperemeter but contributes nothing to the deposition rate.

Layer properties

To determine the adhesion of the layer, a scotch tape test and an adapted wipe test with a cloth was performed. The adhesion regarding the scotch tape test was ok. There, only a small amount of upper molecules was removed from the surface. In
In contrast, the adhesion measured with wipe test was very poor. There, more than half amount of the material was removed. With a wet cloth even the whole layer could be removed, due to the dissolubility of BSA in H$_2$O.

In Figure 6, a fracture of a coated Si substrate is shown in a SEM micrograph. A high layer roughness can be observed. The roughness increases for substrates which are coated with a higher concentration of the initial solution. A possible reason for that phenomenon could be, that the BSA molecules tend to agglomerate already in the solution. Thus, not only single molecules were deposited but also bigger clusters. This effect is notable only for higher concentrations of molecules in the solution.

Figure 6: The SEM micrograph shows the fracture of a coated Si substrate. The Si substrate visible at the bottom is covered by a fully closed BSA layer with layer thickness of about 70 nm.

4. SUMMARY

This paper reports on vacuum deposition of organic molecules by Electrospray ionization (ESI) deposition. The deposition tool was homemade using mainly standard vacuum components. Thin films were successfully deposited using solutions with different concentrations of BSA (2 µM, 20 µM and 200 µM) in a 1:1 mixture of MeOH and H$_2$O. The deposition area has a circular shape with highest deposition rate in the center. The capillary to substrate distance was varied and the influence of on the deposition rate and on the transmitted current was investigated. Deposition rates of up to 32 nm/min and transmitted currents of up to 26 nA were achieved. The layer adhesion was moderate with low material remove by scotch tape test but easily wiping away by wipe test.

REFERENCES