Direct Patterning of Functional Materials via Atmospheric-Pressure Ion Deposition

T.E. Hamedinger[*], T. Steindl[*], J. Albering[**], S. Rentenberger[***] and R. Saf[*]

[*] Institute for Chemistry and Technology of Organic Materials, Graz University of Technology, Stremayrgasse 16/1, 8010 Graz, Austria, thomas.e.hamedinger@tugraz.at
[**] Institute for Chemistry and Technology of Inorganic Materials, Graz University of Technology, Stremayrgasse 16/3, 8010 Graz, Austria
[*] Institute for Solid State Physics, Graz University of Technology, Petersgasse 16, 8010 Graz, Austria

ABSTRACT

Interest in thin films of functional materials has increased enormously in recent years because of the wide range of possible applications. Here we report an experimental setup we have termed Atmospheric-Pressure Ion Deposition (APID) as a novel technique that allows highly controllable and soft processing of various materials (e.g. polymers, bio molecules and inorganic materials) into thin and ultrathin structured films. The technique is based on an electrospray process. Microdroplets are initially formed and dried, generating ions that are extracted by electrostatic lenses. Thin structured films are then produced by the deposition of the resulting ion beam onto a moveable target. The technique offers several interesting features, including precise control of film thicknesses. Experiments investigating structured deposition of various kinds of functional materials are reported. This might provide a simple approach creating thin structured films and composites that are currently unattainable.

Keywords: vapor deposition process, thin structured films, devices

1 INTRODUCTION

The industrial demands for new advanced functional materials have driven the development of thin film technology. Today, thin films are used in a wide range of industrial applications, e.g. (bio)sensors, devices (organic light emitting devices (OLEDs), solar cells, transistors), optical applications and coatings [1]. A still challenging problem is the processing of these materials to thin films with variable and defined chemical composition in all three dimensions. However every single technique that is applied for thin film deposition (e.g. spincoating, chemical vapour deposition) shows limitations: the area that can be coated is limited, the use of solvents often makes the assembly of multilayered systems impossible, and molecular weight of the processed material is limited. Independent of the specific application, it is important to keep in mind that the way these films are produced is often the key to optimal exploitation of the intrinsic potential of the materials involved. To overcome such limitations we have introduced Atmospheric-Pressure Ion Deposition (APID) [2] as a new extremely soft technique that uses the same ionization process as ESI-MS and is capable of processing a large spectrum of materials such as polymers, biomolecules and inorganic materials.

2 EXPERIMENTAL SETUP

APID - an ion beam technique that operates under atmospheric pressure - is based on the electrospray-ionization (ESI) process well known from Mass Spectrometry (MS) [3]. A schematic diagram of the experimental setup is shown in Fig.1.

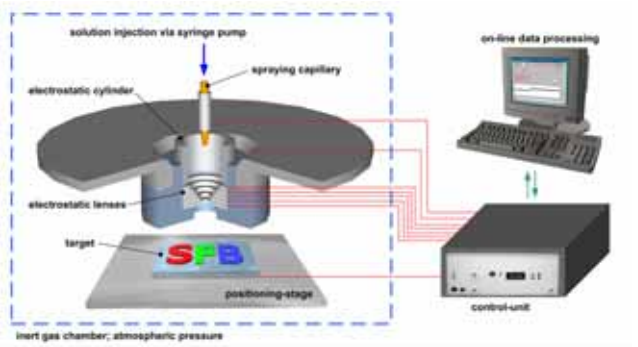


Figure 1: Experimental Setup of Atmospheric-Pressure Ion Deposition

A constant flow of a solution containing the material to be processed is injected into the system through an ESI-MS capillary. The solution leaving the needle is dispersed into an aerosol of charged micro-droplets. In contrast to comparable methods like spincoating these charged droplets are appropriately dried under atmospheric-pressure to produce singly and/or multiply charged ions. The electrostatic lenses are used to extract these ions out of the cylindrical electrode, and to focus the resulting ion-beam towards the target were the ions are deposited.

3 SIMULATION OF ION-TRAJECTORIES

In principle the technique can be divided into two main processes: the electrospray ionisation and the extraction/deposition of ions onto a target. Both can be controlled and monitored in real time. Simulations of ion trajectories with SIMION 7.0 were used to find a suitable

experimental setup where focussing is adjustable. To simulate ion trajectories under atmospheric-pressure conditions it was necessary to implement an additional program that included the collisions of ions with the surrounding gas. The simulation predicts that the electrostatic field close to the first electrostatic lens is responsible for the extraction of the ions and can be tuned without significant effects on the electrospray process.

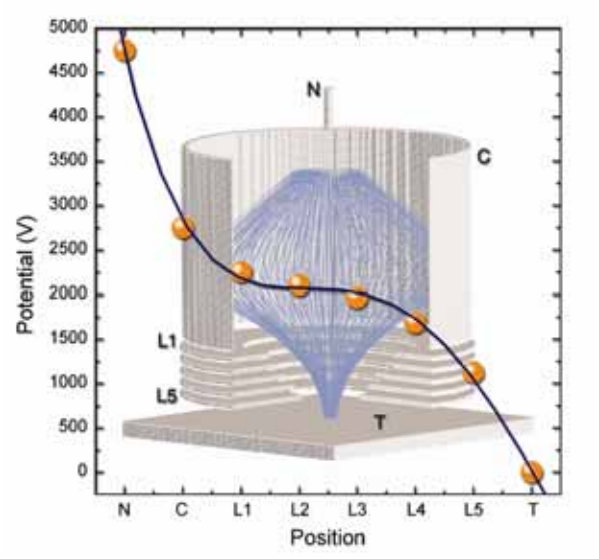


Figure 2: Ion-trajectories simulations with SIMION 7.0 (inset) and potential gradient from needle (N), cylinder (C), electrostatic lenses (L1-L5) to target (T)

Fig. 2 shows a potential gradient from needle to target that was applied during deposition and as an inset a three-dimensional representation of an electrode arrangement. By variation of the potentials applied to the electrostatic lenses and some other process parameters lateral resolutions up to ≈10,000 lines.cm^{-1} which is far beyond a standard laser printer (600 dpi) could be achieved (Fig. 3).

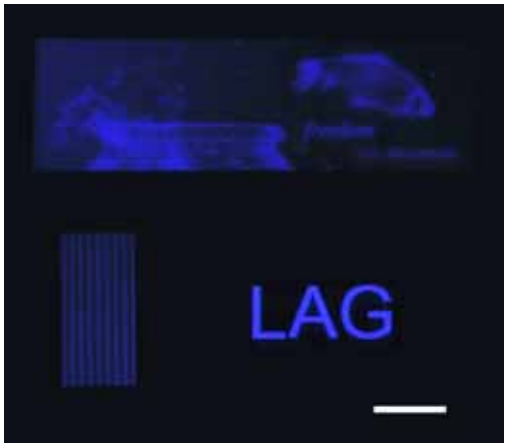


Figure 3: Ultra thin structured films of advanced functional materials with a resolution up to 1,000 lines.cm-1.

Emission photograph of the resulting polymer films (scale bar: 1000 μm).

4 THICKNESS CONTROL VIA MOTION CONTROL

Films having a constant thickness are practically impossible without movement of the target. For structured deposition and exact control of film thickness it was necessary to implement the possibility of target positioning according to given parameters. The algorithm used is shown schematically in Fig. 4.

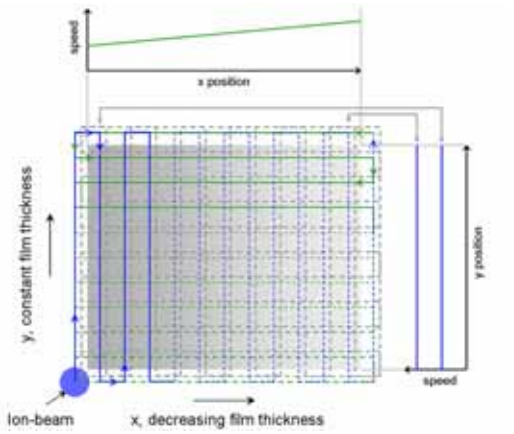


Figure 4: Target movement algorithm

"Line-scans" of the ion-beam, both in the *y*- and the *x*-direction, were performed over the whole area in order to deposit a first "layer". The same algorithm - appropriately shifted in *x* and *y*-direction - was applied to deposit additional layers, as indicated once with the grey grid. During the procedure the speed of movement determined how long the ion beam was positioned over a specific spot, and, consequently, how much material was deposited. This algorithm together with a controlled variation of the speed could be exploited to vary the film thickness in the range of ±1 nm. To facilitate the production of structured films, an additional procedure - that permitted the import of grey-scale pictures, assignment of desired film thickness to individual colors and appropriate translation into stage movements - was implemented into the software (Fig. 5).

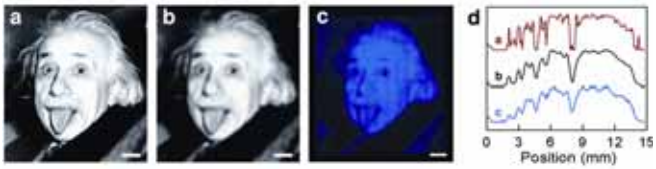


Figure 5: Production of a 3d structured thin film of electro active polymer [2]. (a) An image of Einstein (15x15 mm) was used as template. Grey scales were assigned to desired film thicknesses. (b) Calculation of the image that should be obtained under the assumption of a lateral resolution of 100 lines.cm-1. (c) Emission photograph of the resulted

thin structured film. (d) Comparison of thickness profiles and emission intensity along a horizontal line through the eyes in (a)-(c); scale bar: 2 mm

5 TAILORING FILM MORPHOLOGY

Each application of thin films requires distinct surface properties. With APID it is possible to tailor these properties by variation of different process-parameters (e.g. concentration, flow rate, etc.). To study the effects of these different settings during the APID-processing atomic force microscopy (AFM) measurements in the so-called "tapping-mode" were performed on a Digital Instruments Nanoscpope IIIa AFM under ambient conditions. AFM scanning was performed with a typical scan frequency of 0.5-1 Hz. The images were analyzed and processed using the standard software (Nanoscope V5.12r5) supplied with the control electronics.

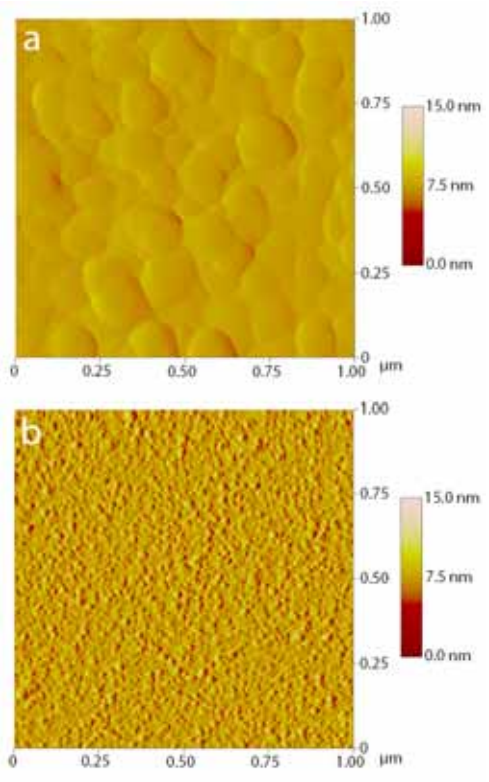


Figure 6: Tailoring surface morphology by variation of process parameters. (a) Thin film of a conductive polymer on ITO/glass with a roughness (r.m.s.) of ca. 0.4 nm (b) Thin film of the same material as in (a) on ITO/glass with a roughness (r.m.s.) of ca. 4 nm.

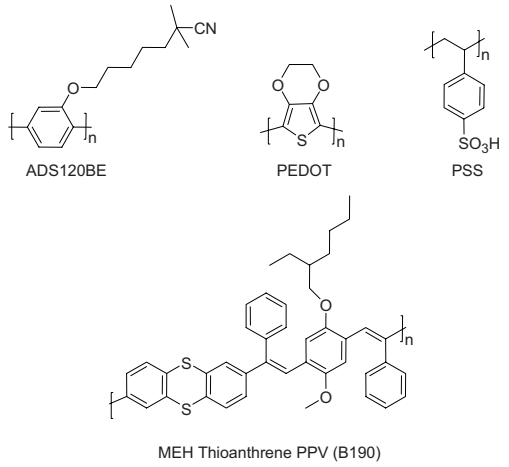
After interpretation of the images taken during AFM measurements two main trends could be deduced. Low concentrations of the material that is processed in combination with low flow rates give very smooth surfaces (Fig. 6a) with a roughness of ca. 0.4 nm (r.m.s.) whereas for high concentration in conjunction with higher flow rates the opposite is the case. During the deposition under these settings films with much rougher surfaces (Fig. 6b) e. g. ca. 4 nm (r.m.s.) are formed.

6 EXAMPLES OF APPLICATIONS

APID allows highly controllable and soft processing of various materials (e.g. polymers, bio molecules and inorganic materials) into thin and ultrathin structured films. Even multi-component systems of materials with comparable solubility can be prepared.

6.1 Multilayered Systems

A polymer multilayer with application in OLEDs was realized by combining spincoating and APID. The used materials are shown in scheme 1.



Scheme 1: Materials used for the multilayered system

A layer with a thickness of around 40 nm of PEDOT/PSS was spincoated out of aqueous solution on an Indium Tin Oxide (ITO) coated polycarbonate (PC) slide. The layer was dried in an evacuated oven for 4 hours at 120 °C. On this intermediate layer a second layer with a thickness of 40 nm of MEH Thiaoanthrene PPV (B190) was brought up by spincoating. The finishing layer of Poly[2-(6-cyano-6-methylheptoxy)-1,4-phenylene)] (ADS120BE) with a thickness of 40 nm was deposited by APID. The polymer was dissolved in a mixture of acetone and distilled water 99:1 (v/v). The whole setup is shown in Fig 7.

Figure 7: Setup of a multilayer system used for OLEDs

The multilayer was characterized before and after deposition of the APID layer. The measurements were performed on a Shimadzu RF-5310 IPC Spectro-fluorometer. The spectra are shown in Fig 8. The emission spectra (full red line) taken after the deposition shows a second peak at 3.1 eV what is characteristic for the material ADS 120BE. The peak of the MEH Thioantrene PPV is slightly shifted to lower wavelengths (2.4 eV) but in form and height identical with the spectra taken before deposition of the APID layer (full black line). The excitation spectra after the deposition (dashed red line) also showed a second peak caused by ADS120BE at 4.3 eV.

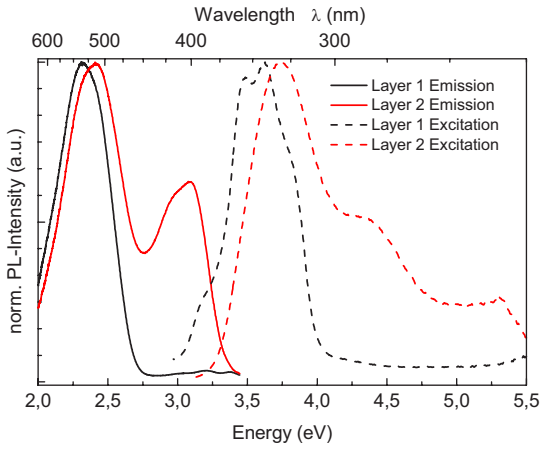


Figure 8: Emission- and excitation spectra of a multilayer system prepared by APID. The red lines show the measurements taken after the APID layer was deposited.

It can be seen, that the deposition of an APID layer does not change the optical properties of the former built up polymer layer. It seems that these layers are neither damaged nor dissolved, what can be seen as an evidence of an existing multilayer structure.

Another example is shown in Figure 9. An antidromic double-wedge consisting of polymers with equal solubility was produced by depositing a film of the blue polymer whose thickness continuously increased into the x-direction followed by a film of the red polymer whose thickness increased into the opposite direction.

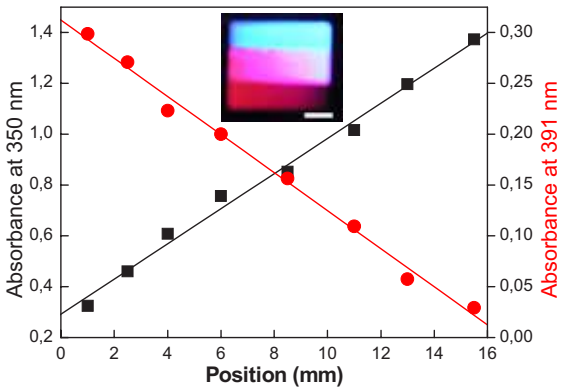


Figure 9: UV/VIS characterization of a double wedge of materials with equal solubility (inset: emission photograph, scale bar: 2 mm)

The graph shows the absorption measured at two wavelengths that correspond to λ_{max} of the two polymers.

Possible applications for structures like this might be found in organic light emitting devices (OLEDs) or in other organic electronic devices like organic field effect transistors (OFETs).

7 CONCLUSION

Direct patterning of advanced functional materials and the production of thin structured films with variable and defined chemical composition in all three dimensions is still a challenging problem. Therefore APID seems promising since being able to use multi-component chemical systems rather simply. We have demonstrated that presently the spectrum of materials that can be processed by this new approach is quite large and should be extended further. Adapted from the electrospray-ionization process APID is a soft technique where usually no chemical modifications will occur. Bearing in mind that APID includes a drying step prior to deposition, even the production of composites impossible today appears to be realistic. Moreover, the technique functions under atmospheric pressure, an important advantage over methods that need expensive vacuum equipment.

8 ACKNOWLEDGEMENT

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