Atmospheric Pressure Ion Deposition – Selected Applications

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ABSTRACT

Within this paper we report new applications with Atmospheric Pressure Ion Deposition (APID), an experimental setup for the processing of various materials into thin structured films under atmospheric conditions. We will show the variety of possibilities and all the benefits which are implicated in this technique, e.g. the simple handling, the wide choice of precursors and substances which can be used and the easy control of morphology, thickness and product stoichiometry.

Keywords: spray process, thin structured films, functional materials, optoelectronic devices, bioactive materials, conjugated polymers

1 INTRODUCTIONS

The interest in thin films of organic functional materials as active components for various applications has continuously increased. Areas of interest are for example, (bio)sensors and electronic devices (organic light emitting devices (OLEDs), solar cells and transistors), optical applications and coatings. Functional materials represent a class of substances that exhibit special properties. In addition for many applications the way how these materials are processed is as important as the chemical structure, especially when several materials are combined to achieve novel properties. Hence, there is a broad interest in new or alternative techniques.

Within recent work we developed 'Atmospheric Pressure Ion Deposition'(APID) (Fig.1) [1].

We continuously focussed on the improvement of the experimental setup of APID and investigated possible applications, especially thin and ultrathin (structured) films of functional materials.

Important advantages in comparison to several other methods are that this technique operates under atmospheric pressure and due to soft processing no decomposition occurs. In addition it is possible to change surface morphology, particle size and simultaneously optical, electrical and structural properties by varying the experimental parameters.

Furthermore the wide choice of matters and an easy control of product stoichiometry and morphology are additional benefits. This technology is able to prepare films with different chemical compositions and structures which provide unique properties in comparison with a bulk material. Results will be presented where APID was used for the production of organic light emitting devices (OLED). Ultrathin films of LiF deposited by APID on top of spin-coated polymer films finally improved the performance of devices. This is a result that opens the way to new devices containing materials that cannot be processed with other techniques. To demonstrate all the advantages and opportunities of this method, new applications in the field of solar cells and bioactive materials as well as thin structured films are shown. APID was applied to improve the performance of the active layer of solar cells, to produce nanoparticle hybrid films with defined composition and to coat electrodes with $LiMn_2O_4$ as a thin film.

The deposited films are reproducible in morphology, uniformity, homogeneity and surface roughness.

Within this paper latest results concerning the application of APID as technology for controlled deposition of materials will be presented.

2 EXPERIMENTAL SETUP

In Figure 1 you can see an experimental setup of APID. A solution injected via a hypodermic needle is dispersed into an aerosol of charged micro-droplets due to high potentials. Thereon the droplets are dried to produce ions and electrostatic lenses are used to extract the ions and to focus the ion-beam onto the target, where the ions are deposited.

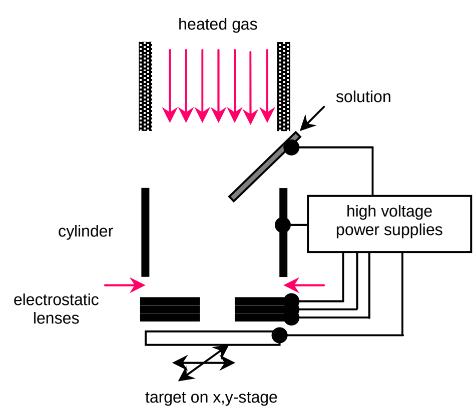

Figure 1: Experimental setup of the APID system

The possibility to produce thin structured films follows from the deposition of the ion beam onto a moveable target

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[1]. In figure 2 you can see the main algorithm, by which the targets get moved. The red and blue lines (solid and dashed) in x- and y-direction, are performed to deposit a first layer; the same algorithm, appropriately shifted, is applied to deposit additional layers (grey grid), for different film thickness and structured deposition the speed of the movement is varied.

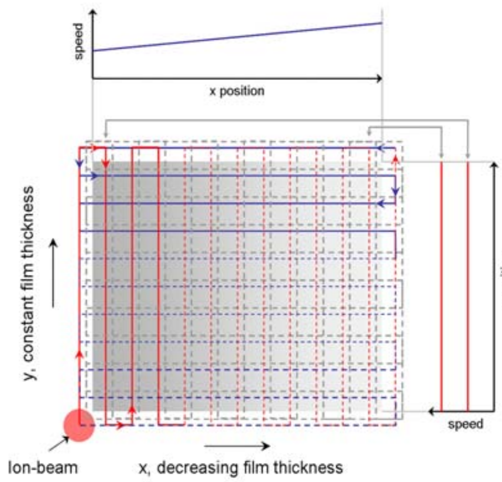

Figure 2: Algorithm applied for the movement of the target [1].

The electrospray ionisation and extraction process can be controlled and monitored in real time.
Basic parameters which give an important impact are a) the flow and the composition of the solution, b) the type of needle applied, c) the temperature and gas flows inside the source, and iv) the potentials applied.

3 EXAMPLES OF APPLICATIONS

3.1 Bioactive Materials

This work was done in cooperation with the Institute of Biotechnology and Biochemical Engineering. Functional coatings and the use of deposited biological molecules like proteins or DNA on appropriate substrates are used increasingly for many applications (biochips). One of our aims was the functionalization of a target on the one hand and immobilization on the other hand. We show the ability to make multilayer systems with different organic materials to modify a glass substrate to immobilize an enzyme on it (Fig.3).

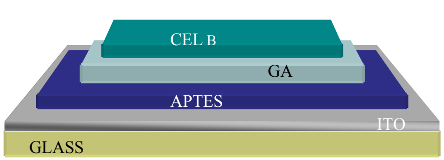

Figure 3: An ITO/glass slide functionalized with a layer of aminopropyltriethoxysilane (APTES) with a thickness of 25 nm, a layer of glutaraldehyde (GA), 15 nm, and on top immobilized enzyme CelB.

After deposition of aminopropyltriethoxysilane and treating with heat the second layer was applied. Each film was investigated by atomic force microscopy (AFM). The thickness of the films were 25 nm (APTES) and 15 nm (GA), with a roughness of 3,0 nm and 3,8 nm. Afterwards the carrier was washed with a PBS-buffer (pH 7) and dried with argon, the enzyme was deposited.

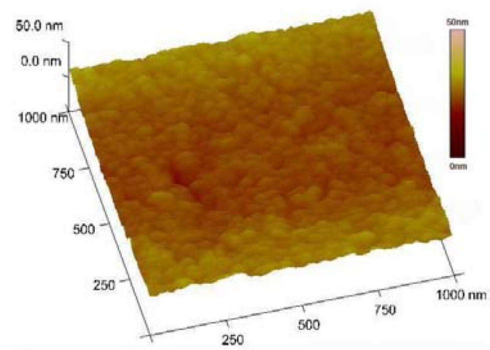

Figure 4: AFM micrographs of a glutaraldehyde layer on an APTES layer.

From a solution of ethanol and H_2O containing a little amount of polyethylene glycol (PEG) the enzyme „CelB“, a beta glucosidase from pyrococcus furiosus, was deposited on this modified substrate by APID in their native form (see Fig. 5). Due to its soft processing their binding-properties were retained. The detection of the activity occurs via reaction of o-NPG (o-nitrophenyl-β-D-galactopyranoside) and measuring the absorption capacity by a defined wavelength.

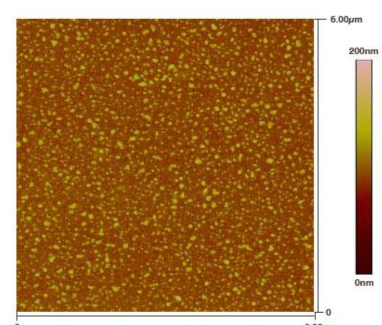

Figure 5: AFM micrograph of immobilized CelB with PEG on modified ITO.

3.2 Solar Cells

Photovoltaics (PV) is a remarkable and sustained growing market. Due to many advantages like flexibility, or low cost production, an increasingly important PV subarea is the field of organic solar cells [2]. Organic PV has attracted attention since a 0.95% power efficient thin film organic cell based on a single donor–acceptor heterojunction was reported by Tang in 1986 [3].
An organic solar cell consists of a so called n-type and p-type material, with good optical absorption and emission

coefficient, and an appropriate band gap. According to the concept of Piber et al. [4] we tried to produce a thin film solar cell consisting of an active layer from inorganic particles and an organic polymer using APID. The preparation was started from solutions containing the appropriate precursor substances. Based on the bulk heterojunction concept layers of nanometer sized inorganic particles of a semiconductor in a polymeric matrix were fabricated. Controlled composition and the control over surface characteristic were obtained. The conversion of the precursor materials occurred during the spraying process on a heated substrate under inert atmosphere.

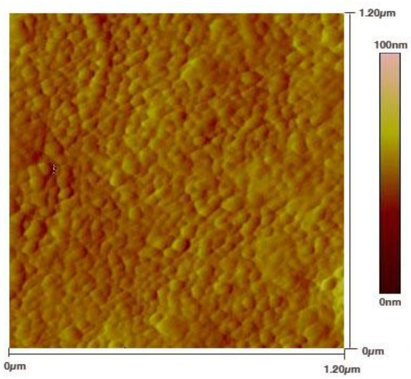

Figure 6: AFM micrograph of an active layer of a solar cell following the bulk heterojunction concept: inorganic semiconducting nanoparticles and organic material.

Furthermore solar cells consisting of an inorganic donor and an inorganic acceptor were built up. The performance of the cell was optimized through variation of the composition of the solution, the solvent, substrate temperature, applied voltage, the flow and the surrounding atmosphere. (Fig. 7: SEM picture of a whole inorganic solar cell.)

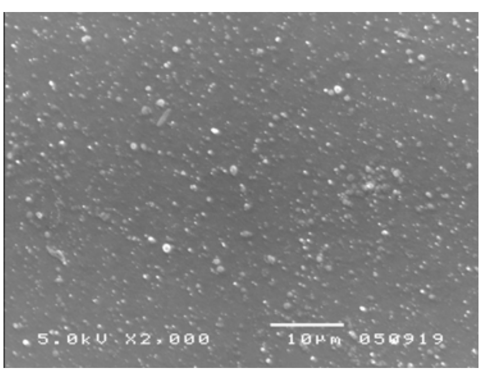

Figure 7: Scanning electron microscopy (SEM) micrograph of a blend of two inorganic materials.

Many deposition techniques that are used to coat electrodes or fabricate films are unspecific in terms of morphology or stoichiometry. Investigations of APID films, by x-ray diffraction and atomic force microscopy, showed that the deposited films were reproducible in morphology and composition.

3.3 Thin Layers of Functional Materials

An opportunity to improve the efficiency of electroactive devices (OLEDs and solar cells) is to cover the active layer with a thin film of LiF. The use of LiF as an insulating layer between the metal cathode and an organic layer had improved lifetimes and quantum efficiency in organic based LEDs [5,6]. The experiments with APID are refered to the deposition of a thin film of LiF with a thickness of about 10 nm to improve the performance of an OLED or an organic solar cell (Fig. 8,9).

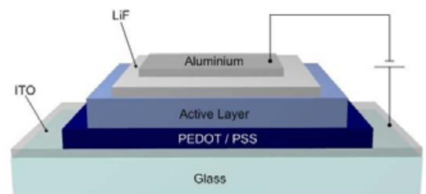

Figure 8: Schematically illustration of the construction of an organic light emitting devise (OLED) with a LiF layer between the Al-cathode and the active layer.

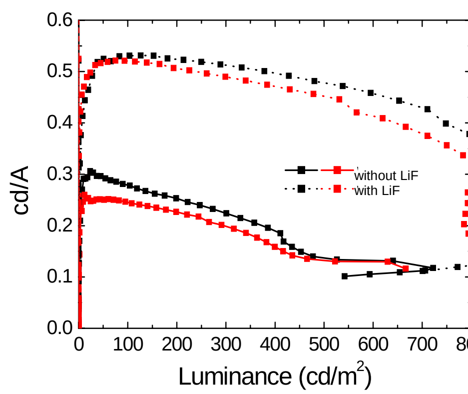

Figure 9: Comparison of the luminance efficiency of two organic light emitting devices with (upper lines) and without (lines beneath) a LiF layer.

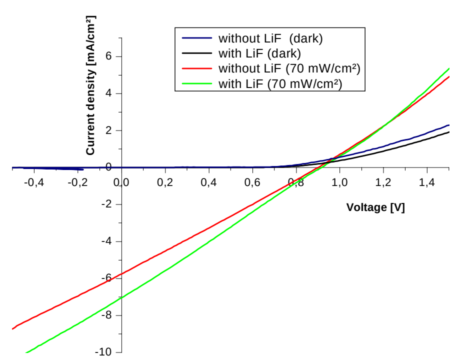

Figure 10: Current/voltage characteristic of a solar cell with and without a layer of LiF.

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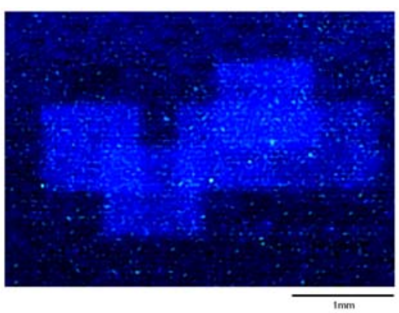
	V_{OC} [V]	I_{SC} [mA/cm^2]	V_{MPP} [V]	I_{MPP} [mA/cm^2]	FF [%]	η [%]
Al	0.9	5.7	0.47	2.8	26	1.9
LiF/Al	0.92	7.0	0.44	3.7	25	2.3

Table 1: Comparison of the characteristic parameters of a nanocomposite solar cell with and without a layer of LiF (10 nm).

The 10 nm thick LiF improved the short circuit current of the solar cell from 5.7 mA/cm² to 7.0 mA/cm².

3.4 Structured Films of Polymers

Conjugated polymer electroluminescence is attracting considerable interest as a technology for use in the lighting, indicator and displays industry. It is a fact that film morphology has an impact on electroluminescence or photoluminescence [7]. One main focus of APID is put on the fabrication of thin (structures) films of light emitting polymers. To demonstrate the ability of our technology you can seen in figure 11 a part of the logo of the University of Technology, deposition of a polymer (1) you see below.



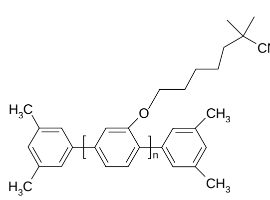


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Figure 11: A part of the logo from the University of Technology.

The spectrum of processing such polymers with APID, which is not shown, reaches from the generation of various polymers as a multilayer system to a blend in a homogenous film to achieve the right features.

CONCLUSION

In conclusion, this technique offers a lot of new perspectives in processing such materials to thin films and/or three dimensional structures. We have demonstrated that Atmospheric Pressure Ion Deposition is a multifunctional technique, which can applied in a wide field of activity: coating of electrodes, fabrication of organic layers or ionic layers for OLEDs and active layers for solar cells, processing of functional polymers or electroactive molecules to mono- or multilayer. Materials, whether it is inorganic or organic, can be used. An important aspect during the processing of materials with APID, which keep in mind, is that degradation reactions can be avoid.

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