FEP

FRAUNHOFER INSTITUTE FOR ORGANIC ELECTRONICS, ELECTRON BEAM AND PLASMA TECHNOLOGY FEP

APPLICATION OF HIGH-RATE PECVD FOR IMPROVED MECHANICAL STABILITY OF ROLL-TO-ROLL MANUFACTURED FLEXIBLE ORGANIC ELECTRONICS

1. Introduction

This paper presents results on the deposition of silicon-containing plasma polymer coatings for applications in the field of organic electronics.

This first part introduces the hollow cathode arc discharge based Plasma Enhanced Chemical Vapor Deposition (arcPECVD), which was used in this research. The deposition geometry is introduced and the effect of two composite process parameters as well as the effect of the monomer flow are discussed.

The second part of the paper discusses the performance of silicon-containing plasma polymer layers deposited using arcPECVD with respect to improved mechanical stability.

2. The arcPECVD process

The hollow cathode can be used to generate an arc discharge that exhibits extremely high electron densities, which makes it very attractive for plasma activated deposition [1] and high-rate PECVD processes. The deposition geometry that was used in this research is based on the hollow cathode unit (HCU) developed at Fraunhofer FEP. A schematic representation of the deposition geometry is shown in Figure 1. The HCU consists of the hollow cathode and a circular anode (primary anode), which is mainly used during the ignition of the plasma. An additional anode (booster anode) is located in the plasma chamber to optimize the position of the high-density plasma with respect to the substrate. The process gas (Argon) is injected through the hollow cathode. Additional gas inlets inject the monomer (here hexamethyldisiloxane; HMDSO) and reactive gas (oxygen), which provide material supply for the coating.

The setup is tested in the roll-to-roll web coaters *labFlex® 200* and *novoFlex® 600* at Fraunhofer FEP. The *labFlex® 200* is schematically shown in Figure 2. This roll-to-roll coater features three deposition chambers. The side chambers are equipped with single magnetrons and the chamber at the bottom can be used for arcPECVD, magnetron based PECVD or dual magnetron sputtering.

Fraunhofer Institute for Organic Electronics, Electron Beam and Plasma Technology FEP

Winterbergstr. 28
01277 Dresden, Germany

Authors

Michiel Top
Phone +49 351 2586-355
michiel.top@fep.fraunhofer.de

Dr. John Fahlteich
Phone +49 351 2586-136
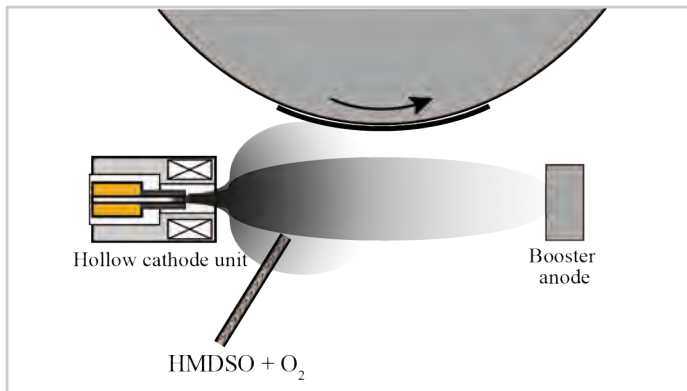john.fahlteich@fep.fraunhofer.de

www.fep.fraunhofer.de

Figure 1. Schematic representation of the arcPECVD deposition geometry.

The *labFlex® 200* allows to test deposition technologies in a dynamic roll-to-roll process with a web width up to 200 mm. The *novoFlex® 600* is equipped with an arcPECVD setup up to 600 deposition width and is described in detail in an earlier publication [2].

Important process parameters include the HMDSO flow, the oxygen to HMDSO ratio and the applied power per unit of monomer flow. The applied power per unit of monomer flow directly related to the applied amount of energy per HMDSO molecule and was found to control the fragmentation rate of the HMDSO molecules as was observed using mass spectrometry. Figure 3 shows two spectra, one with high power and one with low power without changing the HMDSO and oxygen flow. Both spectra were normalized using the Argon peak at 40 amu. The peaks above 50 amu, which were assigned to large fragments of the monomer [3], decrease with increased power whereas the single molecule peaks (e.g. Si and O) increase with increased power. The O_2 peak decreases as well indicating increased dissociation of the oxygen molecules.

Increasing the oxygen to HMDSO ratio increases the number of available oxygen atoms compared to silicon and carbon atoms and therefore has a large influence on the chemical composition. Increasing the oxygen flow changes the chemical structure from a Polymethyldilisoxane-like coating towards a more SiO_2 like structure and thereby changing, for example, the refractive index. This effects was already discussed in detail elsewhere [2].

The HMDSO flow can be used to control the dynamic deposition rate. Increasing the HMDSO flow between 90 and 210 standard cubic centime per minute (sccm) while keeping the ratio between HMDSO flow and power as well as the ratio between HMDSO and oxygen flow constant leads to a change of the dynamic deposition rate from 240 up to 700 nm·m/min (Figure 4). This allows for excellent control of the final coating thickness in a large range independent from the web speed, which is a major advantage for in-line processes.

The slope of Figure 4 (4 nm·(m/min)·sccm^{-1}) was used to calculate the ratio between the number of silicon atoms injected in the chamber and the number of silicon atoms implemented in the coating.

Figure 2. Schematic representation of the labFlex® 200.

Assuming a chemical composition of $SiOCH_8$[2] and a mass density of 1.5 g/cm^3, the slope of 4 mm·(m/min)·sccm^{-1} corresponds to an effective silicon consumption of approximately 67%.

3. Applications for improved mechanical stability

The next part present results for a selection of these applications in the field of organic electronics.

Improved robustness of barrier films.

Organic electronic devices are usually encapsulated using a gas barrier film to avoid the contact with water vapor and oxygen [4]. Typical water vapor barrier materials consists of thin inorganic coatings like SiO_2, Al_2O_3 or $ZnSn_xO_y$ on a polymer substrate These materials exhibit excellent barrier properties but are very brittle and vulnerable to mechanical damage. Roll-to-roll processing of the barrier materials could damage the coating and therefore lead to a reduced barrier performance. Testing of the robustness of thin film coatings can be done using a fatigue test that exposes the coating to simultaneous bending, tension and mechanical contact on the coating side with a roller (Figure 5).

In this test, the left part of the sample is fixed whereas the right clamp is moved up and down. A polished metal roller is placed onto the film surface in the middle and is constrained in the horizontal direction. The red-line indicates the coating and the black line indicates the substrate. Parameters that can be varied include drum weight, drum diameter, speed and the number of cycles.

Within this research, a polished metal drum (3 kg, 38 mm diameter) was used at a speed of 0.1 m/s and at a web width of 220 mm.

---

[2] Based on the chemical analysis in [2]. The hydrogen content is an estimation as there was no direct access to the hydrogen content but has only a limited influence on the final result.
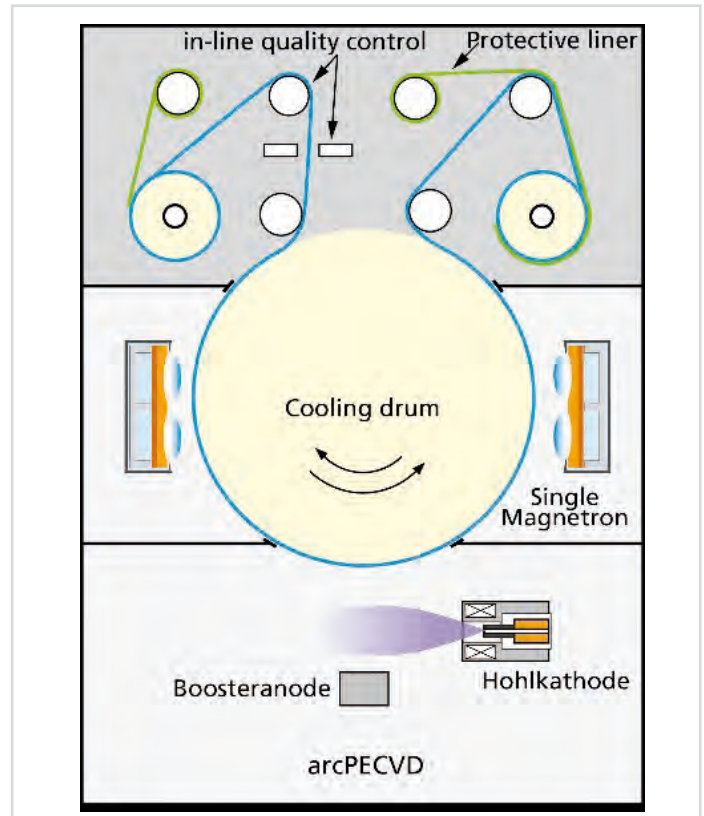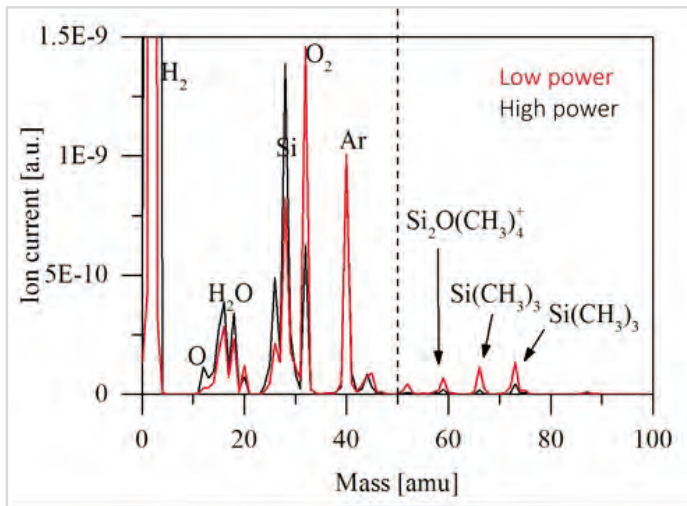
Figure 3. Mass spectra for a low power (red) and high power (black) plasma. The peaks left from the dashed line correspond to single atoms and small molecules whereas the peaks right from the dashed line correspond to large fragments of the HMDSO monomer.
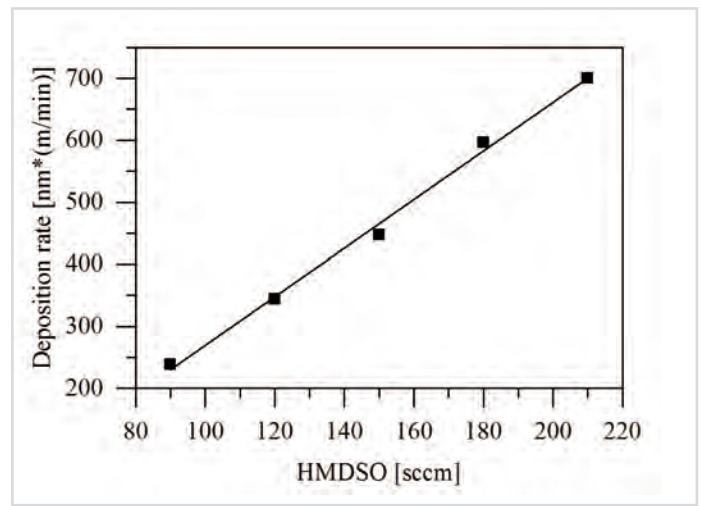

Figure 4. The HMDSO flow [sccm] can be used to tune the dynamic deposition speed [nm·m/min].
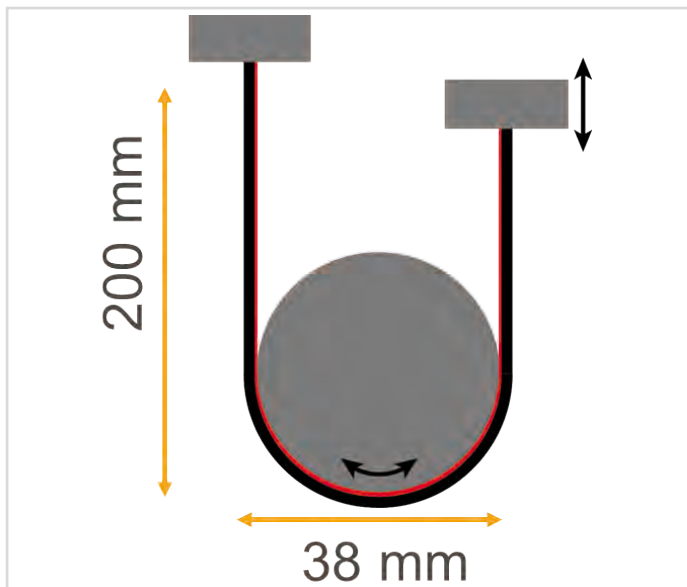

Figure 5. Schematic representation of the fatigue testing system. The red line indicates the coating and the black line indicates the substrate. The left clamp is fixed whereas the right clamp moves up and down.

Figure 6. Effect of the arcPECVD protective coating on the robustness of the barrier coating. The x-axis represent the protective coating thickness whereas the x-axis represents the WVTR before (black square) and after (red dot) the fatigue test.

The fatigue test was used to quantify the effect of the arcPECVD protective coating on the robustness of a 30 nm thick $ZnSnO_4$ sputtered barrier coating. More information on the $ZnSn_xO_y$ barrier coating and the magnetron sputtering technology given in an earlier publication [5]. The different coatings were tested and the barrier performance of the coatings was compared to reference samples without any fatigue test. The barrier performance was tested using and water vapor permeability tester (WDDG, Brugger Feinmechanik) with a measurement area of 78 cm² at a temperature of 38°C and a relative humidity of 90%. Figure 6 shows the results. The x-axis represents the protective coating thickness and the y-axis represents the WVTR before (black square) and after (red dot) the fatigue test. The deposition of the PECVD coating shows no significant change in the WVTR indicating that the process does not damage the barrier coating. The sample without any protective layers is strongly damaged by the fatigue test as the WVTR is 10 times higher compared to the reference value. Applying a 550 nm thick decreases the damage to the coating already with 50% but
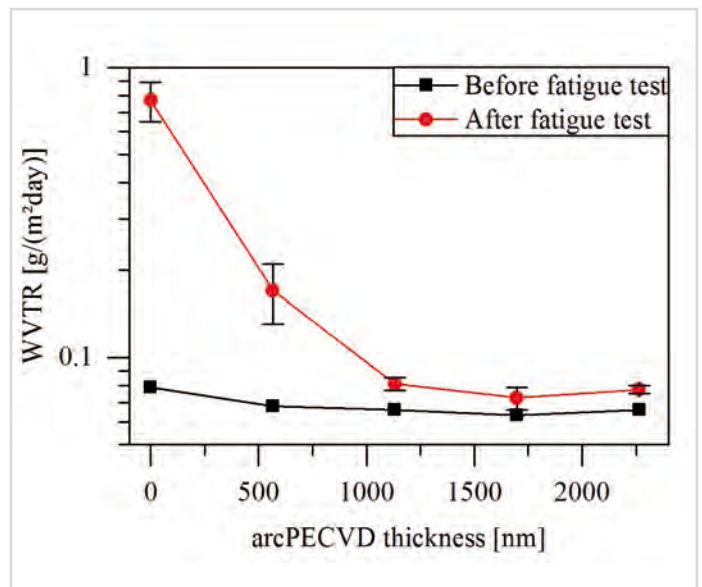
is still not sufficient. For protective coatings with a thickness larger than 1000 nm, there is only a minor increase in the WVTR compared to the reference film.

Adhesion improvement
Encapsulation of organic electronics is usually done by lamination of the barrier film onto the device using an adhesive. To guarantee mechanically stable devices, it is important to provide good adhesion between the barrier coating and the adhesive. Inorganic barrier films usually show low adhesion against organic adhesive materials. A German wheel peel test (Sebastian V) (according to IPC-TM-650) was used to test the adhesion between different coatings and a pressure sensitive adhesive (Adhesive Research EL 92734). The adhesion force between the EL 92734 and inorganic barrier coatings (e.g. $ZnSn_xO_y$ and Al_2O_3) lies between 0.2 and 0.3 N/cm. This is much lower compared to, for example, a PET film (3.1 N/cm). Application of a plasma polymeric coating using arcPECVD allowed us to improve the total adhesion up to 2.5 N/cm.
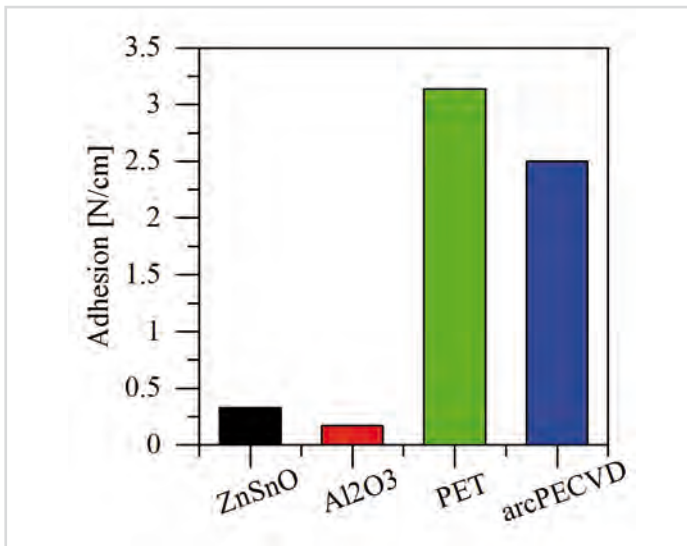
3

Figure 7. Adhesion measurements using a peel test for different coating materials against a pressure sensitive adhesive.
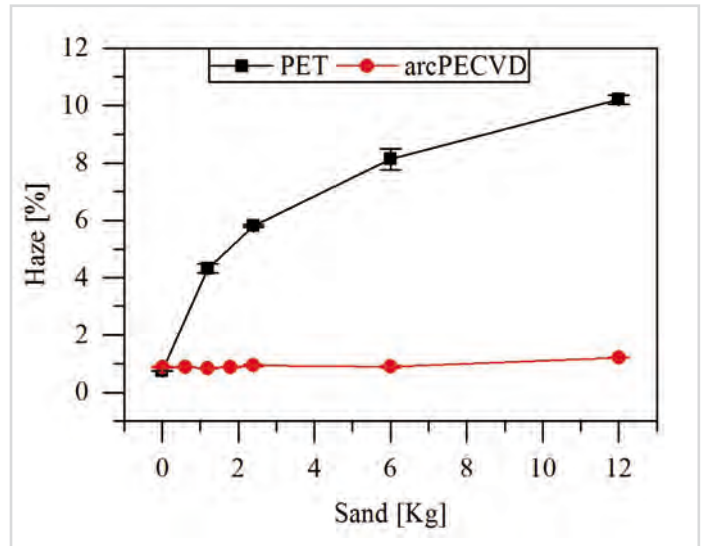

Figure 8. Result of the HAZE measurement. The black squares show the change in haze for the bare PET and the red dots show the change in HAZE for the coated PET.
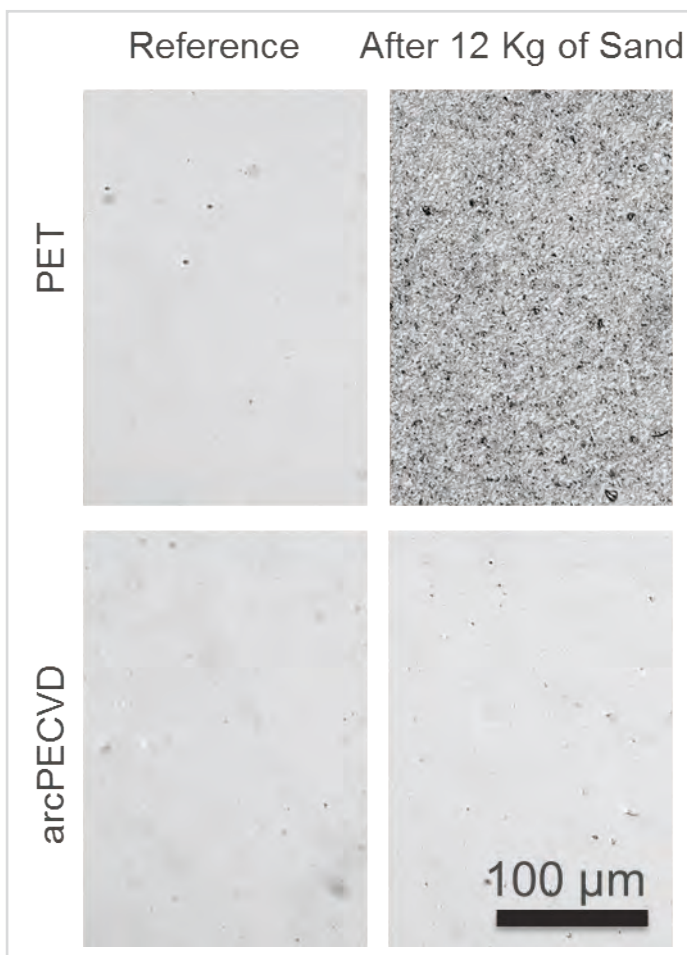

Figure 9. Optical microscope images of the bare PET and coated PET before and after application of 12 Kg of sand.

Resistance against sand trickling

The last application that is presented here is the resistance of arcPECVD coatings against sand trickling.

Within this setup, sand is sprinkled on the surface with a rate approximately 330 g/min. The distance between the holder and the sample is approximately 7.5 cm and the angle of incidence is 42°. Different amounts of sand were tested and the HAZE of the samples was measured according to ASTM D-1003 before and after the sand treatment. Selected samples were investigated using optical microscopy. Figure 8 shows the result of the HAZE measurement. The bare PET substrate shows an increased HAZE starting at 0.7% up to 10.2%. The arcPECVD coating has an initial haze of 0.88% that remains unchanged up to 2 Kg of sand. Increasing the amount of sand to 12 Kg leads to a small increase in the HAZE up to 1.2%. The result is also clearly visible in the optical pictures (see Figure 9 showing an extreme roughening of the PET surface (top right) whereas the arcPECVD coating shows no significant changes (top left).

4. Conclusion

We introduced the hollow cathode arc discharge based PECVD process (arcPECVD) that can be used for the high-rate application of silicon-containing plasma polymer coatings. Changing the HMDSO flow was shown to be an excellent tool for modification of the dynamic deposition rate, which allows for control of coating thicknesses independent from the web speed. Three applications in the field of organic electronics were introduced. Using a silicon-containing plasma polymer coating on top of a thin inorganic $ZnSn_xO_y$ barrier increases the robustness of the coating as well as the surface properties to improve the adhesion against a pressure sensitive adhesive. The last results show that a silicon-containing plasma polymeric coatings reduce the wear due to sand trickling and thereby drastically reducing the increase of HAZE compared to a PET substrate.

References

[1] H. Morgner, M. Neumann, S. Straach, M. Krug, Surf. Coat. Technol. 108–109 (1998) 513–519.

[2] M. Top, S. Schönfeld, J. Fahlteich, S. Bunk, T. Kühnel, S. Straach, J.T. de Hosson, Surface and Coatings Technology 314 (2017) 155–159.

[3] M. Top, J. Fahlteich, De Hosson, Jeff T. M., Plasma Processes and Polymers 14 (2017) 1700016.

[4] C.A. Bishop, Roll-to-roll vacuum deposition of barrier coatings, 2nd edition ed., John Wiley & Sons Inc, Hoboken, New Jersey, 2015.

[5] J. Fahlteich, W. Schönberger, M. Fahland, N. Schiller, Surf. Coat. Technol. 205 (2011) 141–144.