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DEPARTMENT OF PHYSICAL ELECTRONICS

HABILITATION THESIS

2017 **Tomáš Homola**

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Plasma Processing of Surfaces and Nanostructured Coatings for Flexible and Printed Electronics

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RNDr. Tomáš Homola, PhD.

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Author	RNDr. Tomáš Homola, PhD. Faculty of Science, Masaryk University Department of Experimental Physics

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Abstract

Atmospheric pressure plasma processing of thermally sensitive surfaces has recently become a subject of great interest in novel emerging technologies, particularly in the field of flexible and printed electronics. This thesis consists of commentaries on the author's published research papers, which address atmospheric pressure plasma treatments of flexible substrates and plasma processing of coatings on flexible substrates for flexible electronics. It is organized into three main sections: the first provides the background of atmospheric-pressure plasma generation, the second presents plasma pre-treatment of substrates, and the third focuses on plasma post-treatment or plasma processing of coatings on flexible surfaces. In addition, the thesis also briefly summarizes the problematic aspects of flexible and printed electronics and how plasma treatments may contribute to faster, cheaper and more competitive manufacturing comparing to the present state of the art in electronics.

Keywords: plasma treatment, flexible and printed electronics, surface energy, roll-to-roll, mesoporous coatings

Abstrakt

Povrchová úprava teplotně citlivých materiálů atmosférickým plazmatem se stala objektem velkého zájmu v nových technologiích, např. v oblasti flexibilní a tištené elektroniky. Tato habilitační práce pozůstává z komentářů k mým nedávno publikovaným článkům, které se týkají povrchové úpravy flexibilních materiálů atmosférickým plazmatem a vrstev na flexibilních površích pro flexibilní elektroniku. Práce je členěná do troch částí: první část poskytuje přehled zdrojů atmosférického plazmatu, druhá část prezentuje povrchovou úpravu flexibilních substrátů a třetí část se zaměřuje na post úpravu vrstev pro flexibilní elektroniku. Práce rovněž stručně sumarizuje hlavní výzkumné aspekty flexibilní a tištené elektroniky a jak může právě plazma přispět k rychlejší, levnější a víc konkurence schopné výrobě v porovnání se současnými klasickými elektronickými zařízeními.

Klíčové slova: úprava plazmatem, flexibilní a tištená elektronika, povrchová energie, roll-to-roll, mezoporézní vrstva

Preface

Atmospheric pressure plasma and plasma treatment of surfaces is an area of research in which I worked for twelve years. First, I joined Laboratory of Surface Discharge Studies at Comenius University in Slovakia in 2005. Afterwards, in 2008, I enrolled in the doctoral programme in Plasma Physics. Since then, I have continued within the same laboratory, and worked on many interesting projects. Half of my doctoral study was spent as a full-time research Intern at the Singapore Institute of Manufacturing Technology (A*STAR, Singapore), where participated in flexible and printed electronics research using roll-to-roll manufacturing systems. After successful completion of my doctoral study in 2012, I joined the newly-established research and development centre known as CEPLANT (R&D Centre for Low-Cost Plasma and Nanotechnology Surface Modifications) at Masaryk University in Brno, Czech Republic. Since then I have worked on various experimental research topics, dealing preferably with functional thin films, surfaces and plasma treatments.

During 2012 – 2015 I accepted two long-term international internships, at Lappeenranta University of Technology, Finland, and at Joanneum Research in Austria. At Finland, I learned to operate various atomic layer deposition (ALD) systems which I used to deposit TiO_2, Al_2O_3, CeO_2, ZnO coatings. Subsequently, the head of the ALD group in Finland, Prof. David Cameron, joined CEPLANT in 2015 and since 2017 our ALD project related to opto-electronics has received financial support from GACR. The scientific work related to ALD resulted in nine papers published in recognized impacted journals. Furthermore, ALD has become important in flexible electronics, because it enables the deposition of conformal thin films with high precision of thickness onto flat, thermally sensitive or porous/mesoporous substrates. ALD is currently employed largely in high-end applications.

Since 2016 I have been involved in very active and fruitful collaboration with the Brno University of Technology in plasma processing of inkjet-printed coatings for flexible electronics, particularly photovoltaics. Our first collaborative paper was published in 2016 in ACS Applied Materials & Interfaces, IF 7.5. Since then, the team has started work on numerous novel topics. Moreover, our network has expanded to other local and international institutes.

This habilitation thesis summarizes my main research results related to plasma treatments of surfaces for low-cost flexible and printed electronics. It consists of seven papers recently published in international peer-reviewed journals. The final paper included in this thesis has been recently published in a new IOP journal, Flexible and Printed Electronics, which further confirms the novelty and importance of this topic.

Because all my research activities were always completed jointly with others in form of teamwork, I would like gratefully to acknowledge the support of my current and former colleagues and collaborators:

- Prof. Mirko Černák, Prof. David C. Cameron and Dr. Richard Krumpolec of Masaryk University,
- Dr. Petr Dzik of the Brno University of Technology,
- Dr. Linda YL Wu of the Singapore Institute of Manufacturing Technology, A*STAR, Singapore,
- Dr. Martin Kormunda and Dr. Jindřich Matoušek of J. E. Purkyně University in Ústí nad Labem.

I would also like to extend my thanks to my friend Dr. Tony Long (Svinošice) for sharing his experience and helping to further my competence in written and spoken scientific English.

Of course, I must offer my heartfelt thanks to my fiancée Martina for her love, inspiration, patience and support.

Tomáš Homola

27.11.2017 Brno

DECLARATION

I hereby declare that all the work presented in this thesis is original. Wherever contributions made by others are involved, every effort has been made to indicate this clearly, with due reference to the literature and appropriate acknowledgement of collaborative research.

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In Brno, 27.11.2017 RNDr. Tomáš Homola, PhD.

Content

List of figures

List of abbreviations

AFM – atomic force microscopy

CEPLANT – R&D Centre for Low-Cost Plasma and Nanotechnology Surface Modifications

DBD – dielectric barrier discharge

DCSBD – diffuse coplanar surface barrier discharge

DSSC – dye sensitized solar cell

FTO – fluorine doped tin oxide

ITO – indium tin oxide

PEDOT:PSS -- poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate)

PEN – poly(ethylene naphthalate)

PET – poly(ethylene terephthalate)

R2R – roll-to-roll

TCO – transparent conductive oxide

XPS – X-ray photoelectron spectroscopy

List of papers commented upon

[1] **T. Homola**, J. Matoušek, B. Hergelová, M. Kormunda, L.Y.L. Wu, M. Černák, *Activation of poly(ethylene terephthalate) surfaces by atmospheric pressure plasma*, Polym. Degrad. Stab. 97 (2012) 2249–2254. doi:10.1016/j.polymdegradstab.2012.08.001.

[2] M. Kormunda, **T. Homola**, J. Matousek, D. Kovacik, M. Cernak, J. Pavlik, *Surface analysis of poly(ethylene naphthalate) (PEN) films treated at atmospheric pressure using diffuse coplanar surface barrier discharge in air and in nitrogen*, Polym. Degrad. Stab. 97 (2012) 547–553. doi:10.1016/j.polymdegradstab.2012.01.014.

[3] **T. Homola**, L.Y.L. Wu, M. Černák, *Atmospheric Plasma Surface Activation of Poly(Ethylene Terephthalate) Film for Roll-To-Roll Application of Transparent Conductive Coating*, J. Adhes. 90 (2014) 296–309. doi:10.1080/00218464.2013.794110.

[4] **T. Homola**, J. Matoušek, M. Kormunda, L.Y.L. Wu, M. Černák, *Plasma treatment of glass surfaces using diffuse coplanar surface barrier discharge in ambient air*, Plasma Chem. Plasma Process. 33 (2013) 881–894. doi:10.1007/s11090-013-9467-3.

[5] **T. Homola**, J. Matoušek, V. Medvecká, A. Zahoranová, M. Kormunda, D. Kováčik, et al., *Atmospheric pressure diffuse plasma in ambient air for ITO surface cleaning*, Appl. Surf. Sci. 258 (2012) 7135–7139. doi:10.1016/j.apsusc.2012.03.188.

[6] **T. Homola**, P. Dzik, M. Veselý, J. Kelar, M. Černák, M. Weiter, *Fast and low-temperature (70 °C) mineralization of inkjet printed mesoporous TiO_2 photoanodes using ambient air plasma*, ACS Appl. Mater. Interfaces. 8 (2016) 33562–33571. doi:10.1021/acsami.6b09556.

[7] **T. Homola**, M. Shekargoftar, P. Dzik, R. Krumpolec, Z. Ďurašová, M. Veselý, M. Černák, *Low-Temperature (70 °C) Ambient Air Plasma-Fabrication of Inkjet-Printed Mesoporous TiO_2 Flexible Photoanodes*, Flex. Print. Electron. 2 (2017) 035010. doi: 10.1088/2058-8585/aa88e6

1. Low-temperature plasmas for surface treatments

1.1. State of the art

Plasma is, in terms of energy, the highest state of the matter, lying above solid, liquid and gas. During the past two centuries, plasmas have been used in numerous applications, from low-energy plasma lighting systems to high-energy plasma fusion reactors. Possible "natural" encounters with plasma are limited to only a few examples: perhaps the aurora borealis, the aurora australis (northern and southern lights), lightning, and extremely rare red sprites and ball lightning. Plasma may be categorized according to various parameters: temperature, ratio of ions/neutrals, pressure, composition of gas, etc. One of the most crucial of them for wide-spectrum applicability of plasma is its temperature. In natural conditions, low-pressure plasma exists in a non-equilibrium condition, i.e. particles in plasma exist at significantly different temperatures; such plasma is often called *non-equilibrium*, *non-thermal* or *cold* plasma. The contact of cold plasma with material leads to significant changes in the surface without affecting bulk structure. Transition from low pressure to a higher pressure is associated with a higher number of collisions between the particles and consequently to thermalization of the plasma. Outside the laboratory, high-pressure plasma exists in a condition of equilibrium; a typical example is an electrical arc with temperatures reaching several thousand degrees. The contact of such plasma with inert material leads to sudden and profound changes; it is widely utilized in an arc-welding process.

Since the applicability of cold plasma at low-pressure is inappropriate to low-cost and large-area surface treatments in industrial conditions, researchers have been seeking practical ways of preventing the natural thermalization of plasma during transition from low to atmospheric pressure. This may be achieved by *i)* localization of plasma, *ii*) fast gas flows or *iii*) discharges with ultra-short lifetimes. Localization of plasma is typical of corona discharge, which generates plasma in very small volumes, of a few mm^3. Fast gas flows may be found in most plasma jets – although most of them, especially in ambient air, generate plasma of temperatures higher than 150 °C. Cold plasma generation using ultra-short discharges – micro-discharges – is typical of dielectric barrier discharges.

The use of plasma become important in the 1960s in the microelectronic industry, later in other industrial segments, mostly in the lighting that employed popular helium/neon tubes. The number of research papers related to applications of cold plasmas is rising every year and the state of the art of cold plasma progressively more difficult to understand. In

response to the massive quantity of research papers, several reviews have been published focusing on various aspects of cold plasma science. In 2011, D. Pappas [1] presented a comprehensive review of low-pressure plasmas together with the physical background of breakdown voltage, while the paper further describes knowledge of atmospheric plasmas in 1990's, compares the designs of reactors, and discusses the role of species on surface modification. Two road-maps discussing the future potential of new applications in cold plasma science were published in 2012 [2] and 2017 [3] by leading scientists in the field. Also worthy of note is a review of plasma jets by Fanelli et al. published in 2017 [4].

The most recent two decades have seen a plethora of cold atmospheric plasma sources used in a range of applications. **Figure 1** shows total the number of records for the topic "plasma surface treatment" during 1996–2016. The number of research papers is rising because plasma surface treatments enables new fields of application, e.g. in flexible and printed electronics, among many others.

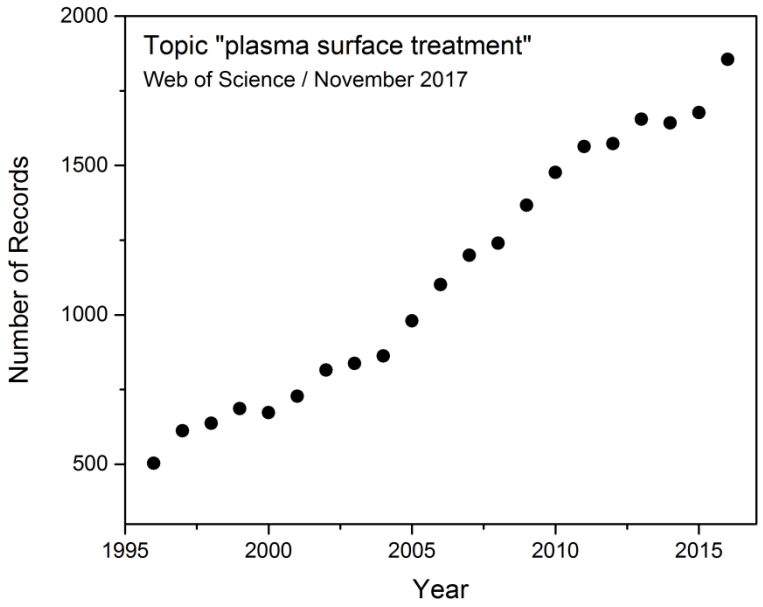


Figure 1. Total number of records addressing the topic of "plasma surface treatment" in the course of the past twenty years. Web of Science.

Dielectric barrier discharges

Dielectric barrier discharge (DBD) is based on the utilization of a dielectric among two metal electrodes connected to an AC (0.05 – 500 kHz) high-voltage (typically up to 10 – 20 kV) generator [5]. The dielectric limits the current and prevents the formation of spark and arc. The dielectric may cover one or both electrodes, or it may be located in the space between

them. Typical materials for the dielectric in DBD are glass, quartz, ceramics and polymers. The inter-electrode distance is 0.1–2 mm. The concept of DBD was introduced in 1857 by Ernst Werner Siemens, who proposed a novel electrical discharge for ozone generation from ambient air [6].

Dielectric barrier discharges generating volume plasma

The first application of dielectric barrier discharge for plasma treatment of material was proposed in 1959 by J.F. McDonald, who used volume DBD to treat polymeric foils [7]. Since then, this concept have been adopted by many research groups and commercial companies and is now widely known as the ”industrial corona”. The industrial corona should not be mistaken for a true corona discharge, needs no dielectric barrier and is generated in a strongly non-uniform electric field near sharp points.

The main feature of volume DBD, or industrial corona, lies in the orientation of the micro-discharges. The micro-discharge event occurs in the volume between high-voltage electrodes and therefore the streamer occurs perpendicular to the electrodes. The treated surface is therefore exposed to plasma that strikes the surface energetically; in extreme conditions, this leads to local damage arising out of overheating. The maximal power in volume DBD is often restricted to a reasonable level. An example of commercial “industrial corona” available the CEPLANT laboratory appears in **Figure 2.**

Figure 2. Commercial volume DBD (“industrial corona”) for roll-to-roll applications, by Ahlbrandt System GmbH. Photo available from www.ceplant.cz.

Dielectric barrier discharges generating surface plasma

It is generally accepted that surface dielectric barrier discharge (surface DBD) was observed and reported for first time in 1958 by Semyon Kirlian, a Russian scientist who was

investigating electrographic plates connected to high-voltage generators. The method he developed is now widely known as a Kirlian photography [8] and can be used to visualize various surfaces, e.g. fingerprints [8,9]. Surface DBD was further improved by Senichi Masuda, a director in a Japanese company that was developing a system for the transport of powder by exploiting electro-charging properties of plasma. A member of his team inadvertently used a power level that was significantly above the standard working parameter, which led to the occurrence of surface plasma. Work on improved surface DBD was published in 1988 by Masuda et al. in a research paper that focused on ozone generation [10]. Afterwards, Masuda founded a company developing ozone generators. Later, Gerhard J. Pietsch and Valentin Gibalov contributed greatly to the further improvement of ozone generation and to the plasma physics of surface DBDs [11,12].

In 2003, Masashi Kando and Mirko Černák (now a professor at Masaryk University and Head of the Department of Physical Electronics) reported the first use of surface DBD to modify non-woven polymer fabrics [13,14], and since then surface DBD has been used to modify polymeric materials many times. Surface DBD plasma in ambient air, used for activation of polypropylene non-woven fabrics, is shown in **Figure 3** [15]. However, long-term use (>100 hours) of surface DBD leads to erosion of the upper electrode system arising out of bombardment by energetic particles from the plasma. This negatively affects overall lifetime and renders its use in industrial applications problematic [16].

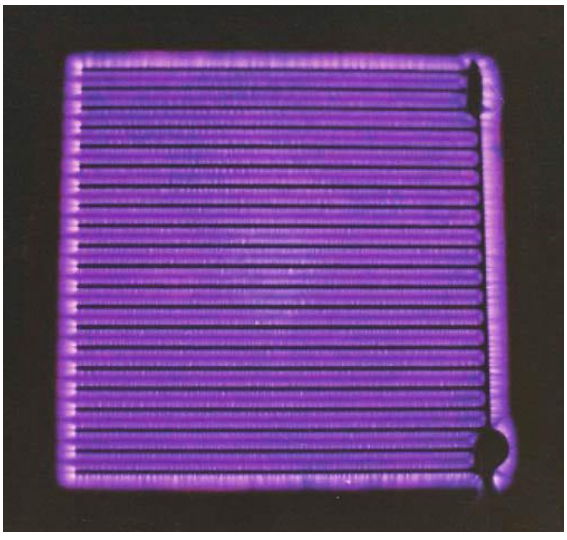


Figure 3. Surface plasma generated by surface DBD in ambient air for treatment of polypropylene non-woven fabrics [15].

Limited lifetime and low levels of safety in the early systems led to a search for a better surface plasma system, one of considerably high energy density with a longer and/or unlimited

lifetime. In late 1990s and early 2000s, the concept of coplanar DBD was already known from flat plasma display panels [17], but the total power delivered to plasma was extremely low, in terms of up to only a few watts [18]. The first high-power coplanar DBD was introduced by Mirko Černák in 2002 [19]. He employed alumina ceramic as a thin (0.4 mm) dielectric and parallel, strip-like molybdenum electrodes (1 mm wide, 50 µm thick, 150 mm long, 0.5 mm strip-to-strip). A surface coplanar plasma with dimensions of approx. 20 × 8 cm^2 was the first system to provide sufficient power, in terms of several hundred watts, thus opening a window for various novel applications.

The concept of coplanar DBD was later adapted by several groups. Novel plasma sources based on coplanar electrode arrangement led to increased energy densities, higher degrees of diffusivity on the plasma and new opportunities for fundamental research. The original inventor and holder of several patents, Mirko Černák, calls the technology "diffuse coplanar surface barrier discharge (DCSBD)". It has been reported that coplanar DBD can operate in a wide range of pressures [20] and generate diffuse, homogeneous plasma at atmospheric pressure in many working gases including: ambient air, hydrogen, oxygen, argon, helium, carbon dioxide, methane, and others. An array of coplanar DBD plasma units available at the CEPLANT laboratory appears in **Figure 4.**

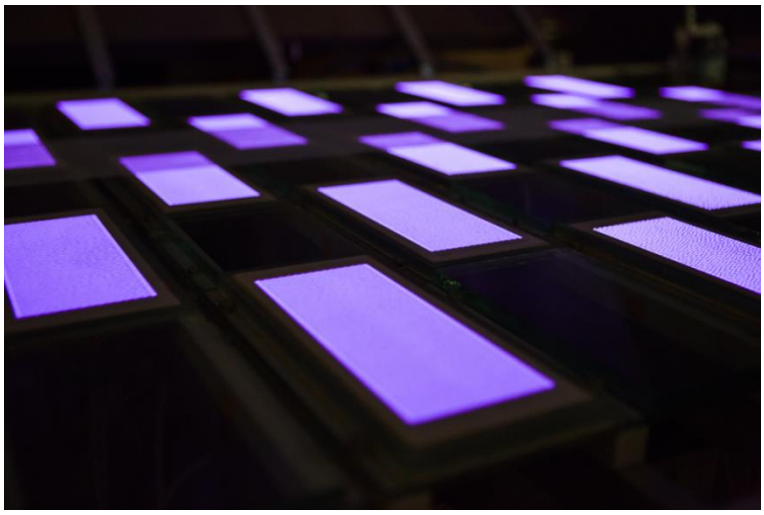


Figure 4. Multiple DCSBD plasma units generating homogeneous plasma operating in an integrated roll-to-roll manufacturing line. Photo available from www.ceplant.cz.

2. Plasma pre-treatment of substrates for flexible and printed electronics

2.1. State of the art

Flexible electronics may be defined as a technology for assembling electronic circuits on flexible substrates. Printing is a common deposition method for mounting electronic devices onto flexible substrates, e.g. screen-, inkjet-, flexo- and gravure-printing [21]. Plastics such as poly(ethylene terephthalate) PET and poly(ethylene naphthalate) PEN foils are the materials most widely-used as flexible substrates. In addition to plastics, thin, flexible glass (Corning and Schott) may be also used for various high-end products. Flexible and printed electronics [22,23] have attracted increased attention in recent times because of their potential to enable low-cost and high-throughput manufacturing of electronics on cheap plastic substrates for various applications, including rollable and foldable displays, smart packaging, photovoltaics, and more.

The primary advantage of flexible and printed electronics lies in their potential for low-cost mass production using roll-to-roll technology. Roll-to-roll, often referred to as web processing, reel-to-reel or R2R processing, may be defined as a process of creating thin films and coatings on flexible substrates in continuous fashion starting with a roll of blank, flexible, thin substrate placed on an unwinder. During the handling of the film, various coating and curing steps take place as the thin film is transported to a rewinder. Roll-to-roll manufacturing may also be combined with non-continuous manufacture, such as roll-to-sheet and sheet-to-sheet processing.

One of the most crucial difficulties (apart from any issues related to printing resolution, web handling, etc.) is the extremely high thermal sensitivity of PET and PEN foils. This limit is established by glass transition temperature and it varies according to density and/or the crystalline nature of the polymer. Thermoplastics such as PET and PEN have low glass transition temperature, less than 150 °C, and therefore cannot withstand the commonly- and largely currently-used deposition procedures, which involve high-temperature curing/annealing/sintering steps. Furthermore, raw plastic materials have poor surface properties (insufficient wettability and poor printability) that often result in coatings of low quality due to a range of defects. This has often been addressed by low-pressure plasma activation; however, low-pressure plasma is barely compatible with atmospheric roll-to-roll systems. Furthermore, industry demands that the entire process should take place in ambient conditions, thus minimizing the cost of the final product and competing successfully with state-of-the art electronics and enabling development of new products and applications.

Atmospheric pressure plasmas have thus become increasingly important for the processing of surfaces and the manufacture of novel products. Applied research into atmospheric pressure plasma is burgeoning, as documented by an ever-increasing number of published papers dedicated to the subject (**Figure 5**).

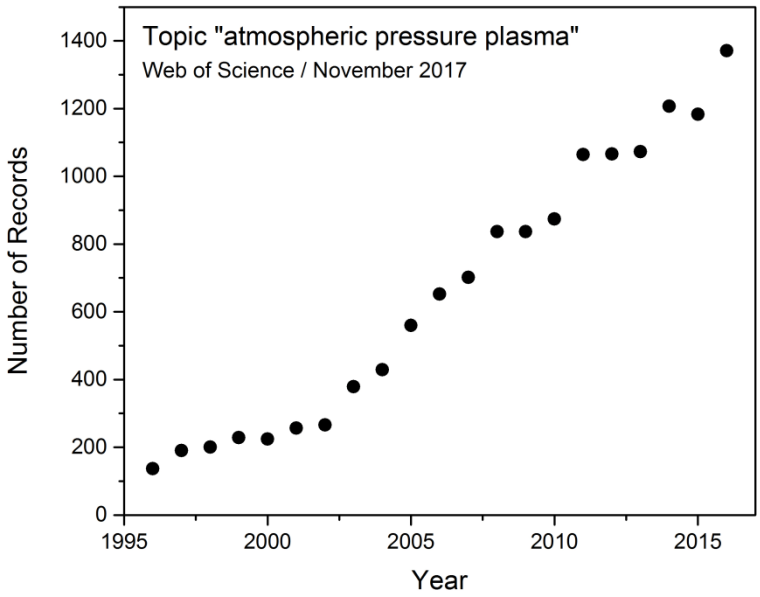


Figure 5. Total number of records addressing the topic of "atmospheric pressure plasma" in the course of the past twenty years. Web of Science.

This part of the thesis summarizes my research work on plasma pre-treatment of substrates for flexible and printed electronics.

- The effects of ambient air plasma on common plastics for flexible electronics such as PET and PEN are reported in ***Refs. 1–2***. Both works were undertaken in collaboration with J.E. Purkyně University, Ústí nad Labem, Czech Republic.
- ***Ref. 3*** provides an introduction to roll-to-roll manufacturing and shows that plasma pre-treatment is beneficial for subsequent coating of PET with transparent conductive films. The entire research work was completed during my internship at the Singapore Institute of Manufacturing Technology, A*STAR, Singapore.
- ***Ref. 4*** discusses the use of plasma for surface treatments of glass and ***Ref. 5*** demonstrates the activation of transparent indium-tin oxide deposited on glass. Results presented in *Refs. 4–5* were completed during my postgraduate study at Comenius University, Slovakia.

2.2. Comments on papers:

[1]

T. Homola, J. Matoušek, B. Hergelová, M. Kormunda, L.Y.L. Wu, M. Černák, *Activation of poly(ethylene terephthalate) surfaces by atmospheric pressure plasma*, Polym. Degrad. Stab. 97 (2012) 2249–2254. doi:10.1016/j.polymdegradstab.2012.08.001.

Number of times cited: 22 Journal IF: 3.4

This article reports on ambient air atmospheric pressure DCSBD plasma treatment of **poly(ethylene terephthalate) PET thin films**. The surfaces were analyzed by water contact angle, XPS and AFM. Water contact angle analysis of PET surfaces before and after plasma treatment appears in **Figure 6Figure 6** and shows that plasma treatment for 1 s leads to a significant decrease of water contact angle, from 78.4° to 40.1°, corresponding to an increase in the polar part of the surface energy and therefore better water wettability. **Figure 6** also depicts hydrophobic recovery of PET surfaces with storage time. The samples were stored under ambient air conditions in a laboratory at a constant temperature of 22 °C and relative humidity of 45%. It is apparent that changes to the surface induced by plasma treatment are not stable and surface modification reverts towards its original state. **Figure 6** shows the hydrophobic recovery effect of PET surfaces treated in plasma for 1 s and 10 s. It is evident that change in the water contact angle is at its most rapid during the beginning of the storage time and reached saturation after approx. 24 hours. The water contact angle of PET treated for 1 s reached 59.9° after 288 hours (12 days). This is, however, lower than the water contact angle measured on untreated samples, which was 78.1°. This hydrophobic recovery is also referred to as the "ageing effect" and it influences the industrial use of plasma-treated surfaces if they are not printed immediately after treatment, e.g. in roll-to-roll processing. Since the declining water contact angle after ageing remains significantly below the untreated value, flexible PET foils may be pre-treated in independent steps and afterwards transported to another line or manufacturing hall for deposition of coating or bonding/laminating with another functional material.

Activation

Detailed chemical analysis of plasma-treated PET surfaces revealed that the reason for the decrease of water contact angle lies mainly in the incorporation of oxygen polar groups during plasma treatment of the PET surface. Since water is a polar liquid, polar groups on the

PET surface lead to better wettability for water or water-based paints and/or functional coatings. Water-based coatings are currently a pressing matter for industry because they are cheap, easier to handle, and without toxic waste, therefore compliant with strict environmental requirements.

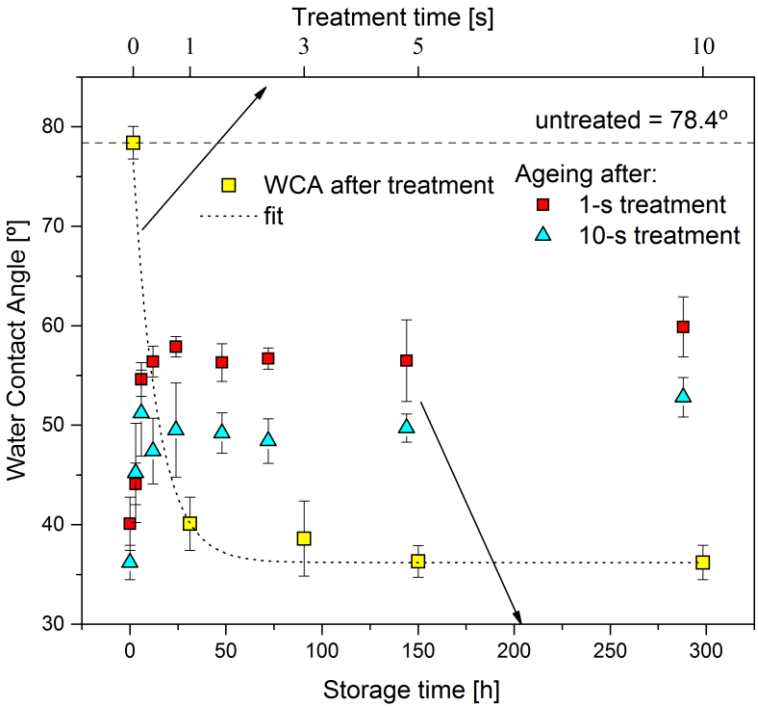


Figure 6. Water contact angles of PET surfaces as a function of DCSBD plasma treatment time (1–10 s) and storage time (0–12 days).

Cleansing and etching

XPS C1s peak analysis showed that the interaction of plasma with PET surfaces leads to a decrease in concentration of C—C/C—H bonds. The C—C/C—H bond concentration indicates the cleansing of the PET surface of hydrocarbons or scission in the PET chain. The cleaning and scission of the PET chain may start simultaneously, but this usually depends on the initial degree of PET contamination: cleansing starts first and, once major contaminants have been removed, plasma interacts with the PET surface. Hydrocarbons (among many other contaminants) adsorbed from ambient atmosphere lead to non-homogeneities in deposited paints and/or functional coatings. The cleansing induced by plasma is therefore beneficial for further surface processing of PET foils.

AFM analysis showed that an untreated PET surface has a flat surface with a roughness of approx. 1.87 nm. Plasma treatment of PET for 1 s led to a significant increase in roughness,

to 6.92 nm. DCSBD plasma treatment therefore provides marked and selective etching of the semi-crystalline polymer. This selectivity arises from the non-uniformly structured bulk, which consists of semi-crystalline, biaxially-oriented PET polymer, i.e. it contains crystalline regions of higher density and amorphous regions of lower density. Since the amorphous part of the polymer is easier to etch than the crystalline, plasma treatment generates surface roughness. Furthermore, a rougher surface at nanoscale contributes to higher adhesion because it can provide a larger area and therefore a higher number of active surface sites for bonding.

[2]

M. Kormunda, **T. Homola**, J. Matousek, D. Kovacik, M. Cernak, J. Pavlik, *Surface analysis of poly(ethylene naphthalate) (PEN) films treated at atmospheric pressure using diffuse coplanar surface barrier discharge in air and in nitrogen*, Polym. Degrad. Stab. 97 (2012) 547–553. doi:10.1016/j.polymdegradstab.2012.01.014.

Number of times cited: 21 Journal IF: 3.4

This paper reports on the ambient air atmospheric pressure DCSBD treatment of **poly(ethylene naphthalate) PEN thin foils**. The surfaces were analyzed in terms of water contact angle, XPS and AFM. Plasma treatment of PEN showed similar effects to those reported for the plasma treatment of PET in the previous paper – *Ref. 1.* However, in addition to ambient air, nitrogen was also used in the plasma treatment of PEN. Comparison between ambient air and nitrogen environments showed that the nitrogen plasma treatment of PEN resulted in slightly lower water contact angles. The water contact angle on an untreated PEN surface was 82.1°, while plasma treatment for 1 s in ambient air and nitrogen led to 30.6° and 28.7° respectively. Ten seconds of treatment time resulted in water contact angles of 25.1° and 18.8° for ambient air and nitrogen respectively. The higher efficiency of nitrogen was explained by incorporation of nitrogen into the PEN structure and, apparently, by the development of nitrogen functional groups.

PET and PEN are the most important and widely-used flexible, low-cost substrates for a wide range of applications in flexible and printed electronics. Both papers published in 2012 showed that DCSBD plasma treatment is a time- and energy-efficient method for surface modification of thermally sensitive polymeric foils and could have the potential to be used in highly improved further processing and manufacturing of flexible electronics.

[3]

T. Homola, L.Y.L. Wu, M. Černák, *Atmospheric Plasma Surface Activation of Poly(Ethylene Terephthalate) Film for Roll-To-Roll Application of Transparent Conductive Coating*, J. Adhes. 90 (2014) 296–309. doi:10.1080/00218464.2013.794110.

Number of times cited: 3 Journal IF: 1.6

This contribution reports on the activation of large-area flexible PET foils for roll-to-roll applications employing transparent conductive poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) coating. A commercial roll-to-roll line from Coatema Machinery GmbH, Germany, equipped with a 1-m web-width roll-to-roll coating and lamination system, was used, consisting of unwinder, web cleaning element, MyPL plasma discharge unit, web alignment unit, slot die coater, thermal oven, web inspection system, lamination unit and rewinder. The roll-to-roll operated at speeds of 1 – 30 $m.min^{-1}$.

The plasma treatments of PET films were carried out using two atmospheric plasma generators: *i)* a commercially available MyPL plasma (AP Plasma, Korea [24]) which was pre-installed within the roll-to-roll line, and *ii)* an experimental DCSBD system provided by Comenius University, Slovakia. MyPL produces diffuse plasma in argon (6000 sccm) together with small amounts of oxygen (30 sccm) that facilitates its reactivity for surface treatments. The DCSBD plasma is described in Section 1. The basic attributes of MyPL and DCSBD plasmas are summarized in **Table 1**.

Attribute	MyPL	DCSBD
Atmospheric pressure	✓	✓
Homogeneity	✓	✓
Ambient air	✘	✓
Argon	✓	✓
Oxygen	✘	✓
Hydrogen	✘	✓
Relative humidity	Up to 90%	Also pure H_2O vapour
Effective area	10 x 1 cm^2	20 x 8 cm^2
Thickness of plasma	3 mm	0.3 mm
Power	75–125 W	350–600 W
Gas temperature	~ 50 °C	~ 70 °C

Table 1. Attributes of, and differences between MyPL plasma and DCSBD, taken from *Ref. 3*.

This study involved three different PET flexible foils, designated as PET 1 (Melinex S, 100 µm), PET 2 (Melinex ST506, 125 µm) and PET 3 (HK31, 125 µm). The PET films were obtained in rolls 500-m and 1000 long, as shown in **Figure 7**. The interaction of MyPL and DCSBD plasma resulted in a significant decrease of water contact angle and an increase in wettability. The decrease of water contact angle accorded with the observations reported in previous papers *Refs. 1 – 2*.

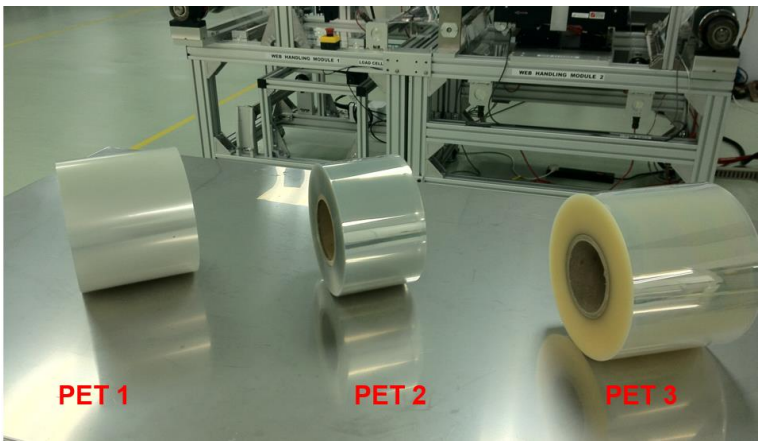


Figure 7. PET 1, PET2 and PET 3 rolls in the Singapore Institute of Manufacturing Technology, A*STAR integrated clean-room laboratory: (complementary material for *Ref. 3*).

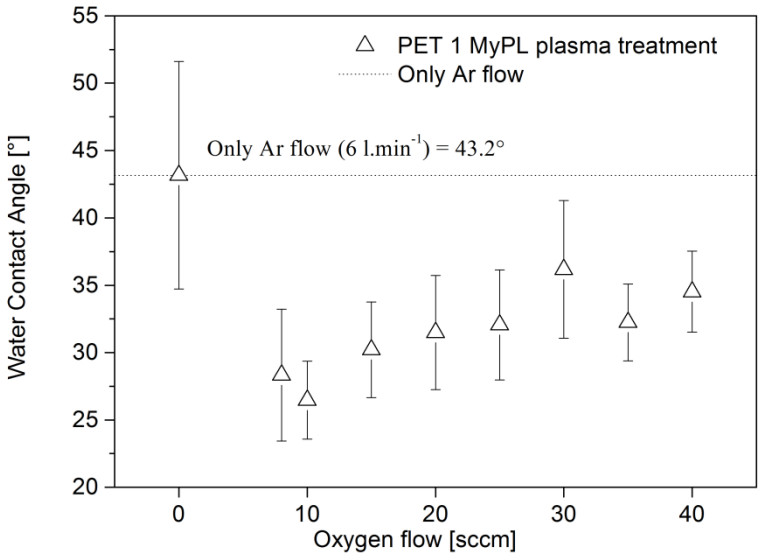


Figure 8. Water contact angles of PET surfaces as a function of MyPL plasma composition (constant argon flow 6 l.min^{-1} + various oxygen amounts in sccm) (complementary material for *Ref. 3*).

Untreated PET 1 foil provided a water contact angle of 80.9°. Pure argon MyPL plasma treatment for 1 m.min^{-1} led to a considerable decrease, to 43.2° ± 8.4° (**Figure 8**). A small quantity (10 sccm) of oxygen admixed with the argon carrier gas had a considerable effect on water contact angle, which then decreased to 26.4° ± 2.9°. It may be proposed that the

difference in plasma efficiency derived from the higher number of oxygen polar groups induced by oxygen in the carrier gas, or a higher rate of etching of surface contaminants arising out of electronegative oxygen. Whatever the underlying mechanism, a small concentration of oxygen was beneficial and decreased both water contact angle and its standard error. Interestingly, a further increase of oxygen had no significant effect on the decrease in water contact angle.

Plasma treatment of transparent, thin polymeric materials also leads to changes in optical properties. **Figure 9** shows transmittance in the UV-Vis-NIR region for PET 1, PET 2 and PET 3 before and after MyPL plasma treatment for 1 $m.min^{-1}$. The plasma treatment clearly led to a slight decrease in transmittance for PET 1 and PET 2. In contrast, the transmittance measured on PET 3 increased. The difference in behaviour and optical parameters among PET foils was explained by their different original surface chemistry: i.e. the PET 3 was chemically pre-treated with silica primer for better wettability, which was also confirmed by XPS.

After MyPL plasma treatment at a speed of 1 $m.min^{-1}$, the PET surface was coated in transparent conductive PEDOT:PSS polymeric film with a thickness of 350 nm and a sheet resistance of 100 Ω/square. Untreated, the PET flexible foil coated with PEDOS:PSS films was visually non-homogeneous and showed various defects – lines and bubbles, as shown in **Figure 10**. The origin of these defects lies in the low surface energy of the PET combined with surface contaminations that led to inferior adhesion between the PET and PEDOT:PSS.

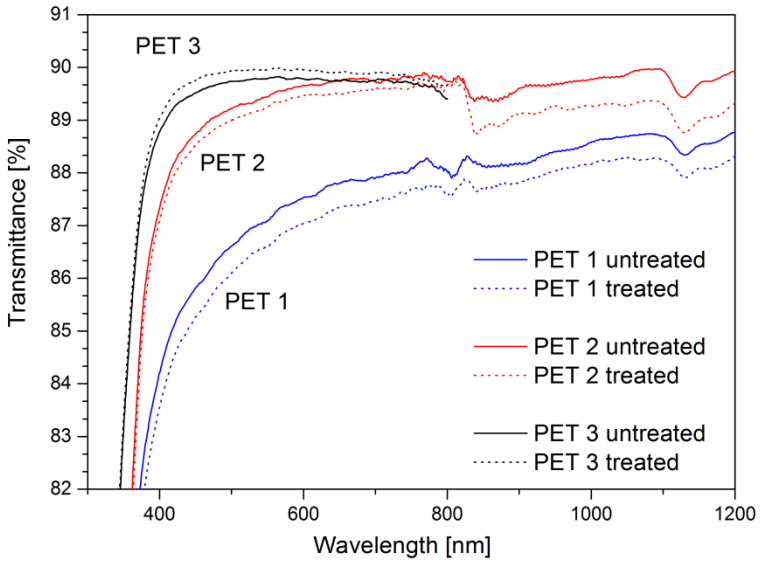


Figure 9. UV-Vis-NIR transmittance spectra for untreated and MyPL plasma-treated PET 1, PET 2 and PET 3: (complementary material for *Ref. 3*).

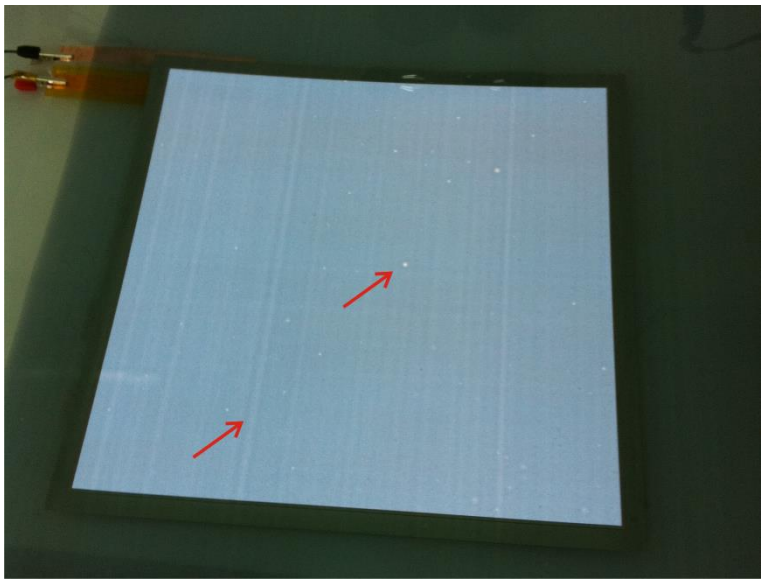


Figure 10. Typical defects, such as bubbles and flow-lines, in PEDOT:PSS coated on untreated PET surface: recorded immediately after coating process, taken from *Ref. 3*.

The concentration of defects in the PEDOT:PSS coating deposited on untreated PET and MyPL-plasma treated PET was qualitatively and quantitatively evaluated by the "Dr. Schenk web inspection system". The data presented in **Figure 11** show the number of defects of severities ranging from minor (1) to major (5). It is evident that plasma pre-treatment of PET prior to slot die coating of PEDOT:PSS led to a significant decrease in the total number of defects in PEDOT:PSS, from approx. 500 to 100.

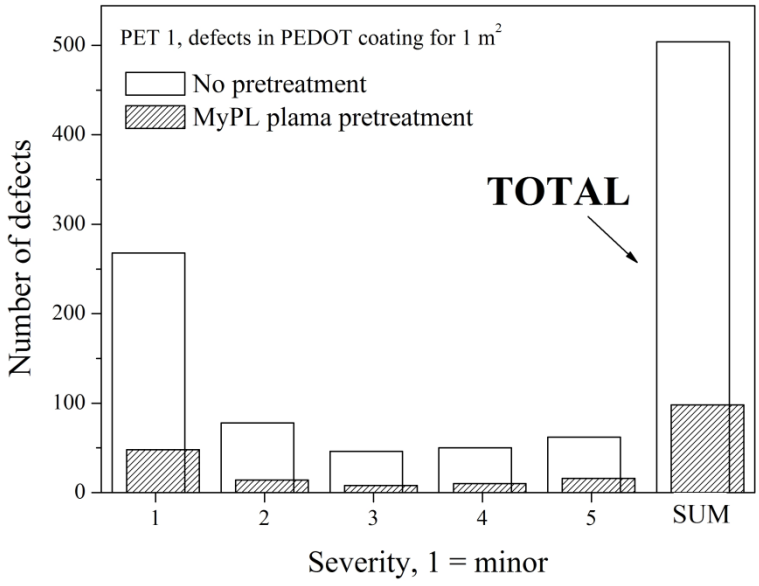


Figure 11. Number of defects in PEDOT:PSS coated on untreated and plasma-treated PET flexible foil, taken from *Ref. 3*.

[4]

T. Homola, J. Matoušek, M. Kormunda, L.Y.L. Wu, M. Černák, *Plasma treatment of glass surfaces using diffuse coplanar surface barrier discharge in ambient air*, Plasma Chem. Plasma Process. 33 (2013) 881–894. doi:10.1007/s11090-013-9467-3.

Number of times cited: 15 Journal IF: 2.4

Since it is capable of withstanding higher temperatures than PET and PEN, glass is also a suitable material for flexible electronics. However, the cost of thin, flexible glass is significantly higher (AF 32 eco flexible glass from Schott AG costs 250 euro per 10 samples of 5 x 5 cm) and it is therefore largely confined to high-end applications. Glass shows excellent transmittance and no haze, making it especially suitable for picture visualization devices such as flexible or rollable displays. In similar fashion to PET and PEN, the surface of glass adsorbs contaminants from the ambient environment and it must be cleaned prior to application of functional films and coatings.

Ref. 4 pertains to a study of the DCSBD plasma treatment of soda-lime glass and the effects of glass on the behaviour of plasma. Since the transparency of light through glass is higher than through PET and PEN, it allows the capture of photographs of the plasma during treatment. DCSBD plasma consists of micro-discharges that create a diffuse and homogeneous layer of surface plasma at full power: 400 W, corresponding to 2.5 W/cm^{-2}. A single micro-discharge consists of a diffuse and filamentary plasma, which varies mainly in the mechanisms of its generation. Whereas filamentary plasma generation is arises out of a streamer mechanism, diffuse plasma is relies upon the Townsend mechanism. This contribution reported that glass placed in close vicinity to plasma leads to suppression of streamer plasma and therefore more diffuse plasma was observed. This was explained by the significant lack of space, insufficient for the electron avalanche to generate the quantity of electrons required to initiate a streamer. Furthermore, the results presented in the paper showed that diffuse and filamentary plasma have different effects on glass surfaces (the visualization was enhanced by hydrophobic amorphous SiO_2 deposited from sol-gel). It was confirmed that diffuse plasma is more beneficial in terms of the development of wettability on a glass surface and this conclusion may also be transferred to other non-conductive surfaces. It should be noted that the lower efficiency of filamentary plasma may also be related to the lower “thickness” of its streamers because the filaments are farther from the treated surfaces. Nevertheless, this is also beneficial for the plasma treatment of any thermally-sensitive material, because filaments

generally contain plasma of higher temperatures, unfavourable to the treatment of such extremely thermally sensitive materials as ultra-thin (<100 μm) polymeric foils. The paper also shows that the effective distance of the treated surfaces from the DCSBD ceramic is approx. 0.1–0.3 mm, which is under, or equal to, that of the thickness of the plasma.

Short plasma treatment of soda-lime glass surfaces resulted in a swift decrease of carbon from 15 at. % to approx. 4 at. % Prolonging the plasma treatment time had no additional effect on the concentration of carbon, probably due to ultra-fast adsorption of carbon from ambient air during transportation of samples between plasma treater and XPS load-lock. Plasma treatment units isolated from ambient atmosphere within dry nitrogen glove boxes are currently being developed by our team at Masaryk University, Brno. These will permit the team to study plasma-treated surfaces and their interaction in a controlled atmosphere, i.e. plasma treatment in dry air or hydrogen followed by immediate storage in inert gas.

In similar fashion to that described in the previous studies of plasma treatment of PET and PEN (*Refs. 1–2*), surface modification of soda-lime glass developed hydrophilicity related to the incorporation of oxygen polar groups combined with cleaning of the surface. In 2014, the author presented a contribution to the Nanocon conference in Brno [25] which demonstrated improved TiO_2 coating adhesion on plasma pre-treated soda-lime glass.

[5]

T. Homola, J. Matoušek, V. Medvecká, A. Zahoranová, M. Kormunda, D. Kováčik, et al., *Atmospheric pressure diffuse plasma in ambient air for ITO surface cleaning*, Appl. Surf. Sci. 258 (2012) 7135–7139. Doi:10.1016/j.apsusc.2012.03.188.

Number of times cited: 41 Journal IF: 3.4

Indium-tin oxide (ITO) is an important semiconductor; it embodies a unique combination properties, among them excellent light transmission in the visible spectrum, good conductivity, and relatively high work function. In flexible electronics, ITO is widely used as a transparent electrode (usually as an anode) in energy harvesting and light-emitting systems. Its high work function enables its widespread use as a hole injection layer and/or electron blocking layer in both energy-harvesting and light-emitting systems. The electrical and optical properties of devices utilizing ITO are sensitive to the surface conditions of ITO. The work function of ITO which, for instance, determines carrier injection efficiency into organic layers,

is extremely sensitive to contaminants. Even a low concentration of adsorbed carbon on an ITO surface may lead to higher turn-on voltages and/or lowered durability and luminous efficiency.

In *Ref. 5* the effects of ambient air DCSBD plasma on ITO (ITO-coated glass) surfaces as well as the effect of ITO on the behaviour of plasma were investigated. As is evident from the previous paper (R*ef. 4*), a glass substrate placed in close vicinity to DCSBD plasma leads to suppression of filamentary plasma and expansion of diffuse plasma. The interaction of DCSBD plasma and ITO glass leads to the total extinction of filamentary plasma, as shown in **Figure 12**. When a conductive ITO surface is exposed to an electrical field, it acts as an electrode with floating potential. The observed extinction of the filamentary plasma in gaps smaller than 0.75 mm bears a certain resemblance to the behaviour of standard-volume DBD burning between two dielectric-coated electrodes in dry atmospheric-pressure air at approximately the same values of inter-electrode gap widths [26]. The method presented in this paper shows a simple method of avoiding filamentary streamer plasma in coplanar dielectric barrier discharges.

The effect of the plasma treatment on ITO accorded with the previously presented results in *Refs. 1–4*. A very short treatment time, of a few seconds, led to a rapid decrease of carbon from 51 at.% to 11 at.%, also associated with a considerable decrease in water contact angle from 84° to <5°. The decrease of water contact angle was explained by cleansing of carbon and oxygen contaminants and incorporation of functional polar groups. Damage to the surface after plasma treatment was negligible. The importance of ITO surface conditions prior to the application of functional coating is discussed in Section 3.

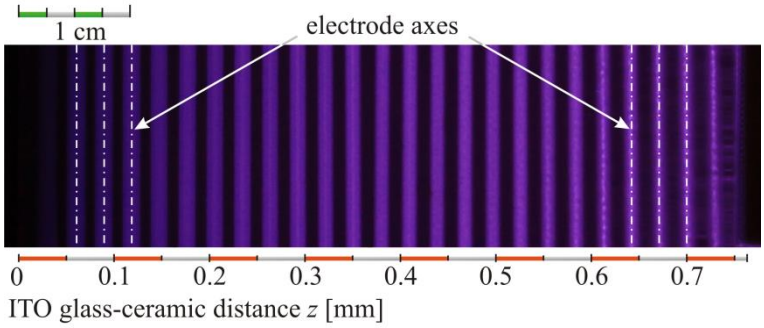


Figure 12. Interaction between ITO and DCSBD plasma followed by total extinction of filamentary plasma in a gap smaller than 0.75 mm, taken from *Ref. 5.*

In addition to the study in *Ref. 5*, our team recently published a paper entitled *Enhancement of electrical properties of flexible ITO/PET by atmospheric pressure roll-to-roll plasma* [27]. This work focuses on the plasma treatment of ITO deposited on flexible PET and

the effects of plasma on the electrical properties of ITO. As reported in *Ref. 5,* it was also confirmed that plasma treatment led to a swift decrease of carbon followed by a decrease in water contact angle. We examined the efficiency of plasma generated in various gas compositions from pure nitrogen to pure oxygen, as well as various ratios between nitrogen and oxygen and including synthetic air. The effect of plasma on ITO work function was also investigated. It is interesting that samples stored in the controlled environment of a dry-nitrogen glove-box exhibited a slower ageing effect, which confirms our hypothesis that moisture and contaminants present in ambient atmosphere contribute to the degradation of surfaces treated by plasma. It was also confirmed that plasma treatment decreased the sheet resistance of the ITO surface. Most of the laboratory work presented in reference [27] was carried out by my postgraduate student Mr. Masoud Shekargoftar, who joined our team in 2016.

3. Plasma post-treatment of coatings for flexible and printed electronics

3.1 State of the art

Flexible and printed photovoltaics can contribute greatly to increasing global access to cheap energy. Dye-sensitized solar cells (DSSC) [28–31] and perovskite solar cells [32–35], in which the photo-electrochemical system relies upon a mesoporous TiO_2 layer, have emerged as a promising low-cost photovoltaic technology and constitute a notable application field for semiconducting photoanodes. Other suitable applications for photoanodes involve, for example, photocatalytic treatment of water [36,37], hydrogen production [38,39], energy storage [40] and various sensing systems.

Titanium dioxide (TiO_2) photo-electroactive layers have already been deposited by a range of techniques in both gas and liquid phases. Deposition from liquid is popular, since the manufacturing equipment required is relatively simple and often compatible with ambient conditions. An example may be found in TiO_2 sol-gel (titanium[IV] isopropoxide, water, hydrochloride acid and ethanol) deposition by spin-coating, dip-coating or spraying. After deposition, the coating must be cured to facilitate solvent evaporation. This is usually performed in an oven at 60 °C for 20 min. The coating is then visually homogeneous, containing no defects, and consists of pure amorphous TiO_2. However, amorphous TiO_2 is electrochemically inactive and the coating has to be further sintered towards crystalline TiO_2,which has photocatalytic attributes. All crystalline forms of TiO_2 (anatase, rutile, brookite) are photocatalytically active, although explanations for the variations in photocatalytical efficiency remain largely lacking [41–43]. The temperature that is required to reach crystalline structure in amorphous TiO_2 is higher than 400 °C [44]; this is completely incompatible with all plastic low-cost flexible substrates. Such incompatibility also applies in other deposition techniques, such as chemical vapour deposition (CVD), atomic layer deposition (ALD) and plasma-enhanced CVD and ALD.

This „temperature" problem may be overcome by utilizing pre-fabricated anatase nanoparticles deposited on a surface, together with a binder from the liquid phase. However, the viscosity and density of the binder must meet the requirements of common deposition methods such as spraying [45], screen-printing [46], gravure printing [47], blade coating [48], slot die coating and inkjet printing [30,49,50].

Numerous works in which TiO_2 mesoporous layers have been employed in photovoltaics have reported the use of coating formulations that need to be either *i)* thermally

sintered at temperatures higher than 150 °C [51] or *ii)* low-temperature sintered (UV and/or plasma) for quite some time (more than 30 min) [52,53]. These high temperatures preclude the use of such fabrication procedures for thermally sensitive substrates [54], such as flexible plastics, while slow, low-temperature curing, employing UV or remote plasmas, involves problems when fast/low-cost roll-to-roll manufacturing is envisaged. In particular, the deposition of TiO_2 photoanodes on PET/PEN foils, with all its significant potential for applications in printed electronics, has emerged as a considerable challenge.

It is generally accepted that plasma treatment of surfaces leads to modification of several nanometres of material (specifically, 20 nm for polymers). Since functional coatings are usually thicker (100 nm and more), traditional plasma treatments affect only the top of the surface whereas the remainder of the bulk remains in its original state. Such treatments would effect only minor or negligible changes and such a procedure also fails to induce any crystallization. These statements are based on my own negative results (unpublished) obtained when attempting high-power-density low-temperature plasma curing of sol-gel TiO_2 coatings during my placement at the Singapore Institute of Manufacturing Technology. I have tried various procedures (different chemical synthesis, ultra-thin multi-coatings, and extremely long treatment times) and all of them have proven inapplicable to flexible electronics. I then began to work on non-compact, porous and mesoporous coatings of the very high-specific surfaces currently used in photovoltaics: mesoporous TiO_2 layers are commonly used in DSSC, as well as perovskites. A hypothesis that DCSBD surface plasma might be generated *within* the coating has been confirmed by pilot results, arising out of research performed in collaboration with Dr. Petr Dzik from the Faculty of Chemistry, Brno Technological University, Czech Republic.

Refs. 6 and *Ref. 7* show the results of this collaborative work on low-temperature plasma processing of functional mesoporous TiO_2 photoanodes deposited on glass sheets and flexible PET foils.

3.2 Comments on papers

[6]

T. Homola, P. Dzik, M. Veselý, J. Kelar, M. Černák, M. Weiter, *Fast and low-temperature (70 °C) mineralization of inkjet printed mesoporous TiO_2 photoanodes using ambient air plasma*, ACS Appl. Mater. Interfaces. 8 (2016) 33562–33571. doi:10.1021/acsami.6b09556.

Number of times cited: 1 Journal IF: 7.5

This work reports on the plasma processing of a TiO_2 mesoporous coating consisting of pre-fabricated TiO_2 anatase nanoparticles (25 nm) embedded in a methyl-silica binder. The binder was chosen in the light of previously reported work [55] because it enables excellent printability on a number of surfaces while preserving a mesoporous structure. Although methyl-silica emerged as a good binding material, the methyl groups on its surface do not support electron transport and therefore the entire coating is of low electrochemical activity. Typically, the coating can be sintered in an oven at 400 °C or cured by UV for several hours to allow removal of organic methyl groups, or treated in high-power-density air plasma. This process is generally known as mineralization and an example of mineralization via air plasma is visualized in **Figure 13**.

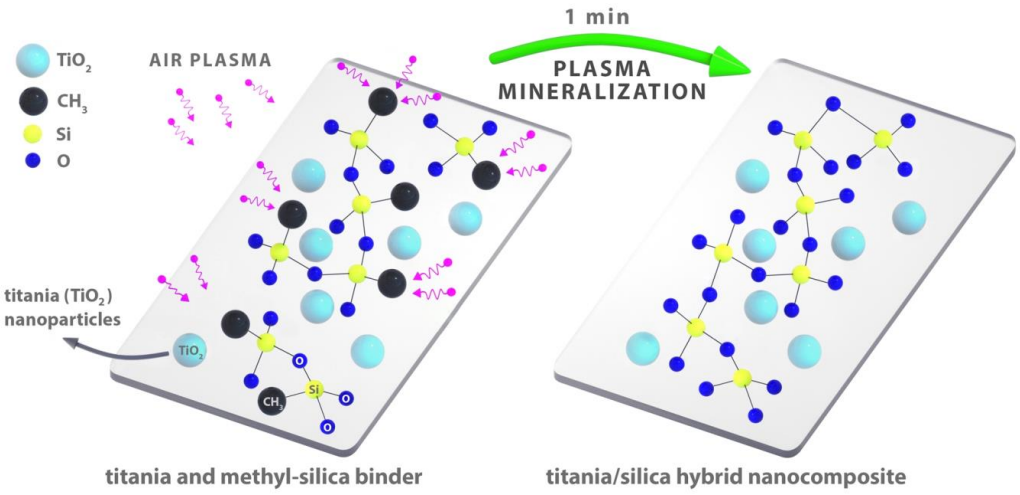


Figure 13. Visualization of plasma mineralization process in ambient air, taken from *Ref. 6*.

The results presented in *Ref 6.* show that rapid DCSBD plasma treatment leads to mineralization of a binder of superior performance to that of binders traditionally sintered or cured by thermal or UV processes. Since mineralization is associated with swift removal of carbon, it may be determined by using XPS to measure the carbon. **Figure 14** shows a comparison of the concentration of elements in a coating deposited on glass after traditional thermal sintering in an oven at 400 °C for 64 min, UV curing for 64 min, and low-temperature plasma treatment for 64 s. All three procedures led to removal of carbon, i.e. mineralization through oxidation of methyl groups. Thermal sintering decreased carbon from 21.6% to 8.9% after approx. 1 hour. An hour of low-temperature UV curing was less efficient; it decreased the atomic concentration of carbon to only 15.4%. In sharp contrast, low-temperature mineralization by plasma treatment decreased the atomic concentration of carbon to 5.7% in approx. 1 min. The maximum decrease, ceasing at approx. 5%, may also be explained by the

reasons given in *Ref. 4* – transportation of the sample in ambient atmosphere may have led to adsorption of carbon contaminants from the air.

Furthermore, thermal and UV treatments lead to an increased concentration of sodium. This is clearly because Na^+ ions migrate from the bulk of the glass onto the glass surface and/or farther into the TiO_2 coating. Sodium decreases the photocatalytic activity of TiO_2 and the migration of sodium ions is often addressed by adding a 100-nm dense SiO_2 crystalline interlayer deposit between substrate and TiO_2 coating [56]. Crystallization of dense SiO_2 is associated with the same temperature issues as crystalline TiO_2 and is scarcely applicable to thermally sensitive, flexible coatings. The coating treated with DCSBD plasma showed no sodium.

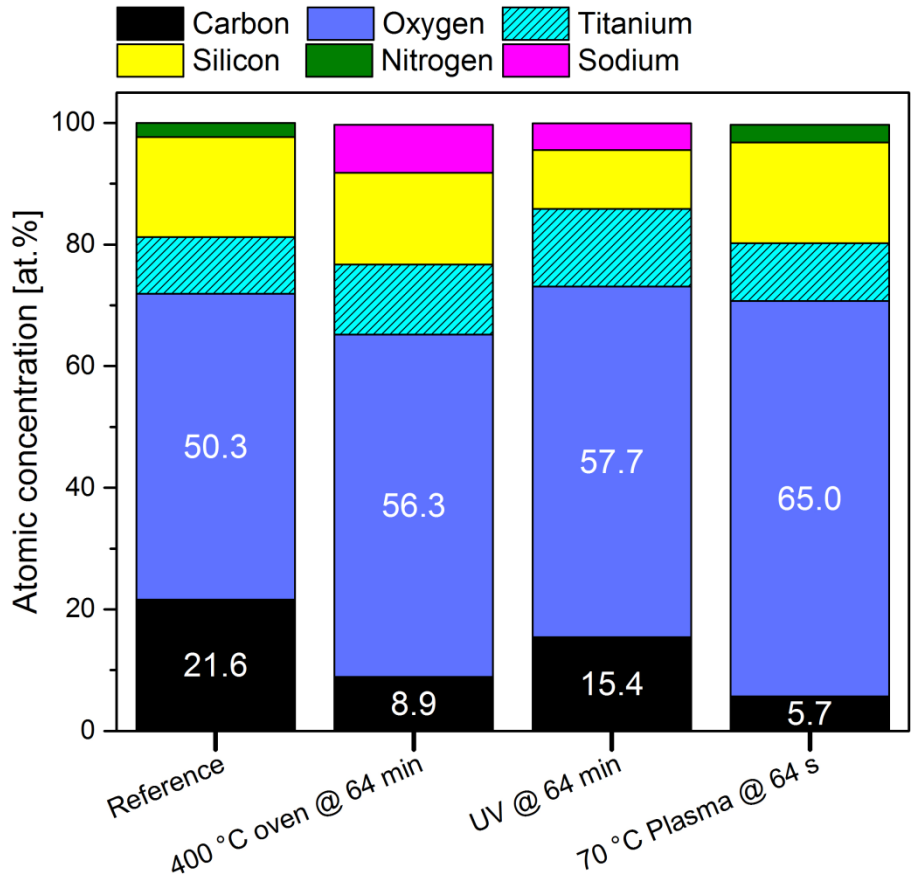


Figure 14. Atomic concentration of elements in a TiO_2/SiO_2 mesoporous coating fabricated using thermal sintering, UV curing and plasma treatment (complementary material to *Ref. 6*).

Ref. 6 shows results relating to the plasma mineralization of TiO_2/SiO_2 coatings as characterized by a range of experimental techniques, including profilometry, SEM, FTIR, BET, XRD, XPS (including C1s, Ti2p peak analysis), linear sweep voltammetry, chronoamperometric measurements and photocatalytic tests. The results may be summarized as follows:

- Plasma mineralization is faster than traditional thermal and UV procedures and because of the low temperature of plasma, only 70°C, it may be applied in the manufacture of flexible electronics (FTIR, XPS).
- Plasma-mineralized mesoporous coatings showed increases in generated photocurrents with respect to plasma treatment time, as shown in **Figure 15**.
- Plasma mineralization has no significant effect on the bulk structure of mesoporous coating (SEM).
- Plasma mineralization has no significant effect on TiO_2 nanoparticles (XRD).

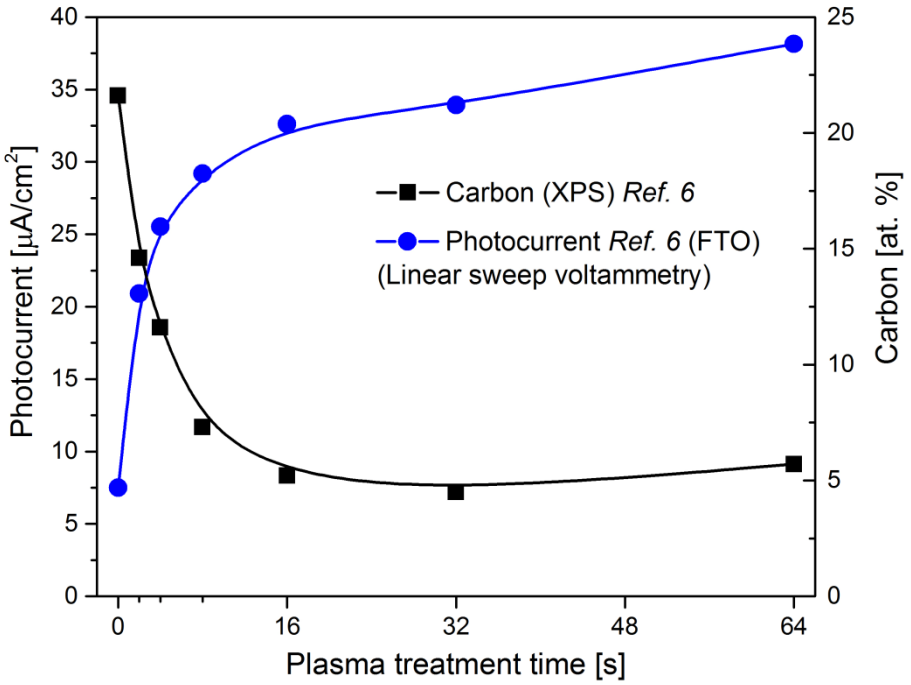


Figure 15. Evolution of total current measured on TiO_2/SiO_2 photoanodes deposited on FTO glass together with total carbon concentration in the TiO_2/SiO_2 coating, taken from *Ref. 6.*

[7]

T. Homola, M. Shekargoftar, P. Dzik, R. Krumpolec, Z. Ďurašová, M. Veselý, et al., *Low-Temperature (70 °C) Ambient Air Plasma-Fabrication of Inkjet-Printed Mesoporous TiO2 Flexible Photoanodes*, Flex. Print. Electron. 2 (2017) 035010. Doi: 10.1088/2058-8585/aa88e6.

Number of times cited: 0 Journal IF: N/A – new journal

Ref. 7 addresses a combination of plasma pre-treatment of ITO film on PET foil (ITO/PET) and plasma post-treatment of TiO_2/SiO_2 mesoporous coatings deposited on ITO/PET. While working with DCSBD plasma in recent years, my colleagues and I noticed that treatment

of lightweight materials, such as polymeric foils, was rendered problematic by difficulties associated with electrostatic charges generated on the material surface. These led to attraction of the treated material towards the plasma and consequently to contact between the treated material and the DCSBD ceramic. Thus the ambient-air gap between the treated material and the DCSBD ceramic has a tendency to shrink to zero, leading to plasma extinction. As a solution to this problem, CEPLANT has developed, thanks to the contributions of Prof. Mirko Černák, Dr. Jozef Ráheľ and Dr. Dušan Kováčík, a pilot roll-to-roll plasma treatment apparatus with concave-curved ceramic DCSBD electrodes. Since the plastic foil can be stretched over the roller, the distance between foil and DCSBD ceramic remains constant and stretching forces compensate for the force from the electrostatic charges.

The team found that short plasma treatment of ITO is important prior to application of a TiO_2/SiO_2 mesoporous coating. Untreated ITO exhibited poor TiO_2/SiO_2 wetting, resulting in an “orange-peel texture”, an undesirable phenomenon. Plasma pre-treatment of ITO/PET for 2 s removed most of the carbon contaminants and generated electronegativity, also important for keeping the work function as high as possible. Interestingly, XPS analysis confirmed that oxygen contaminants were present on the ITO surface, which were also removed from its surface by plasma. After the plasma treatment, most of the oxygen present on the surface was bound to tin and indium in amorphous and lattice structures.

Figure 16 visualizes roll-to-roll plasma processing of a mesoporous coating on flexible ITO/PET foil. The foil is treated by curved DCSBD plasma mounted in close vicinity to the roll with PET foil. This set-up can be further upscaled, e.g. the speed of the line may be increased by adding another plasma unit, and so onwards.

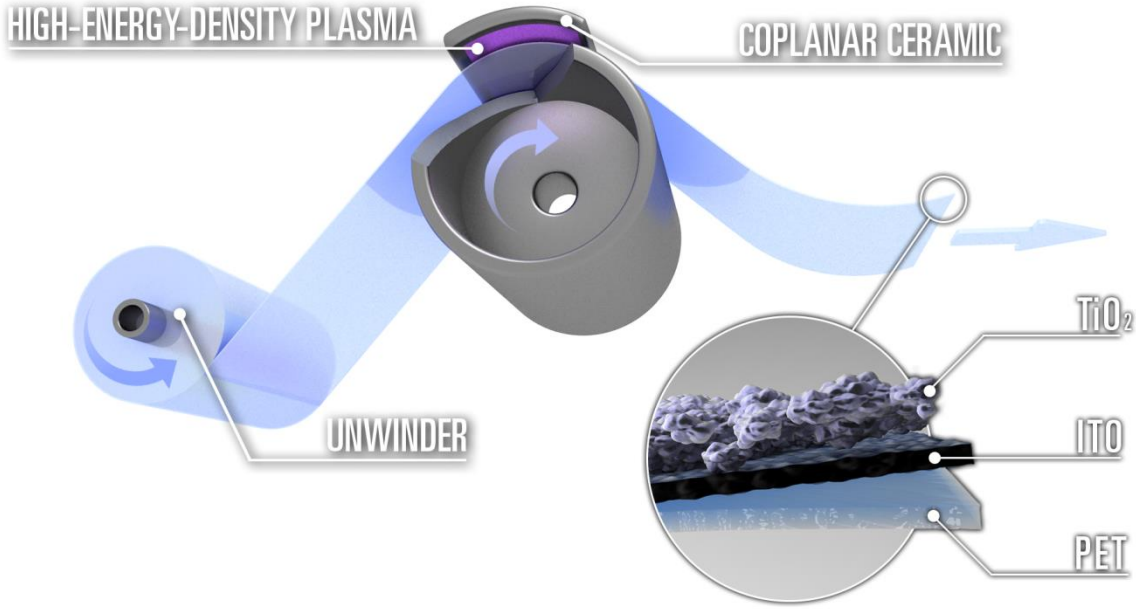
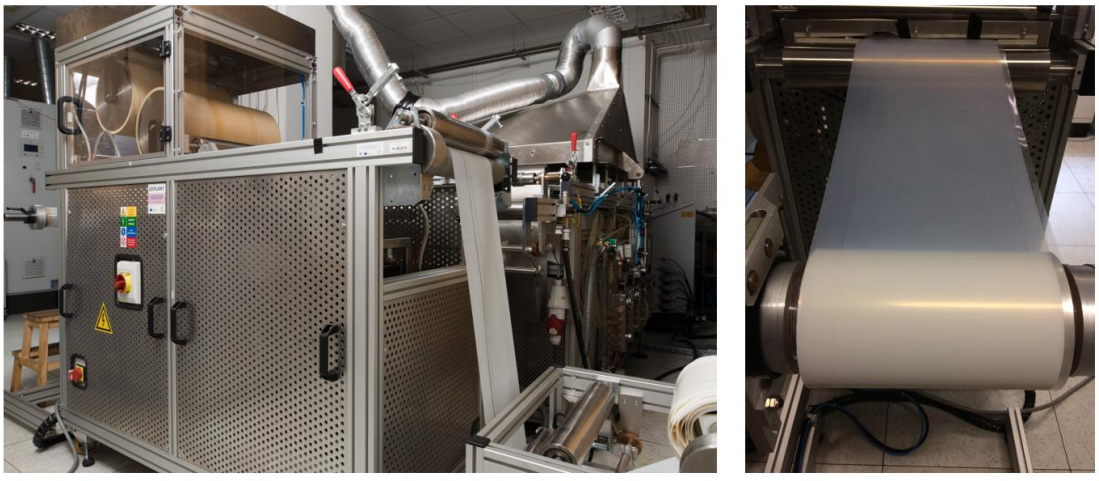


Figure 16. Visualization of plasma fabrication of large-area mesoporous TiO2 photoanodes by roll-to-roll processing.

The apparatus for roll-to-roll treatment of flexible materials developed by CEPLANT appears in **Figure 17**. The large-scale photoanodes were pre-printed at VUT (Brno University of Technology), on a commercial Coatema printing line and afterwards the roll with the photoanodes was treated on a roll-to-roll plasma line at Masaryk University. The plasma line enables treatment of both sides at speeds ranging from 1 to 30 $m.min^{-1}$, fully comparable with standard industrial processes.



a) **b)**

Figure 17. a) Roll-to-roll system at Masaryk University developed by CEPLANT, b) detailed view of TiO_2 mesoporous film on PET roll treated by the roll-to-roll system.

Figure 18 shows fully-mineralized 1 cm^2 flexible photoanodes on ITO/PET foil. The coating maintains good mechanical stability on the flexible substrates. We are currently designing a system for studying coating parameters under various bending conditions.

Figure 18. TiO_2/SiO_2 hybrid nanocomposite flexible photoanodes inkjet-printed onto ITO/PET foil, taken from *Ref. 7*.

Figure 19 shows the effect of plasma mineralization on total atomic concentration (at. %) in TiO_2/SiO_2 coating deposited on flexible ITO/PET. **Figure 19** also compares total current measured on TiO_2/SiO_2 deposited on FTO glass [40] on flexible ITO/PET. The lower currents measured in flexible photoanodes were explained by the higher sheet resistance of ITO.

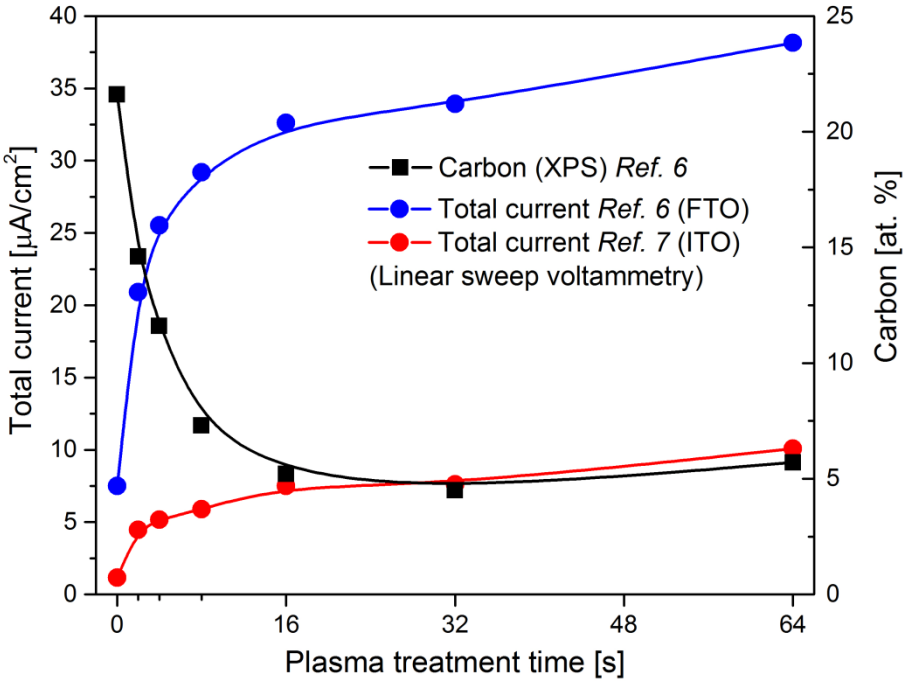


Figure 19. Evolution of total current measured on TiO_2/SiO_2 photoanodes deposited on FTO glass and ITO together with total carbon concentration in the TiO_2/SiO_2 coating, taken and merged from Ref. 6 and Ref. 7.

4. Conclusions

This habilitation thesis presents an extended summary of plasma treatment methods for the fabrication and manufacture of low-cost flexible and printed electronics. I concentrated my attention largely upon:

- plasma pre-treatment of flexible polymeric substrates,
- plasma processing of mesoporous TiO_2 photoanodes created on flexible ITO/PET foils.

It is clear that low-temperature diffuse coplanar surface barrier discharge (DCSBD) plasma in ambient air is capable of efficiently removing organic contaminants from flexible surfaces and also of mineralizing mesoporous coatings by means of removing organic moieties from a binder while preserving its mesoporous structure. This approach may be extended in the future to cover other organic binders and a number of other nanoparticles, among them ZnO and WO_3.

Plasma processing provides production performance superior to those techniques currently considered standard (thermal sintering and UV curing), taking only a fraction of the time required for them at far lower temperatures and making it particularly suitable for incorporation into roll-to-roll fabrication units. This method could constitute an important and major step forward in the large-scale manufacture of photonic devices, among many other applications.

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Appendix: Copies of papers commented upon