Large-area open air plasma sources for roll-to-roll manufacture

High-power density surface plasma generated by diffuse coplanar surface barrier discharge

Tomáš Homola, Jakub Kelar, Mirko Černák, Dušan Kováčik

1 Introduction

The current manufacture of emerging thin-film technologies often does not meet the requirements of low-cost steps enabling commercialization. The future next-generation flexible and printed electronics lies in the deployment of functional thin films over large areas, preferably on low-cost, flexible substrates such as thermoplastics and paper or even nanopaper. Roll-to-roll (R2R) manufacture is a powerful technique to satisfy the need to sequentially deposit various layers over large areas in a continuous fashion. However, the temperature at every single fabrication step is crucial and cannot exceed a threshold given by the substrate or other previously deposited layers, which traditionally must be cured/sintered at an elevated temperature at exposure times incompatible with R2R length/speed. Low-temperature and atmospheric plasmas can provide an excellent way for rapid treatment of polymers and sintering of (nano)layers at low temperatures (< 150 °C), all in open-air conditions without the need for cumbersome and expensive chambers. In this contribution, we present high-power density surface plasma based on coplanar dielectric barrier discharge (DBD) compatible with R2R lines, tested in the application of hydrophilization of polymers and surface cleaning of transparent electrodes in thin-film solar cells.

2 Dielectric barrier discharges: history and present status

The history of dielectric barrier discharges (DBDs) dates back to 1857, when Ernst Werner Siemens constructed the first ozoniser [1] based on an oxygen or air atmospheric discharge – today known as (coaxial) volume DBD, schematically shown in **Fig. 1a**, showing the planar set-up for simplicity. Since then, surface and coplanar geometries of the DBDs electrode systems have been introduced (**Fig. 1b** and **1c**, respectively), which generate a thin layer of surface plasma of considerably higher spatial power density than in volume DBD. The concept of DBDs lies in a dielectric placed between metal electrodes powered by alternating high voltage (frequencies typically ranging from 0.05 to 500 kHz; typically 5 – 20 kV peak-to-peak) [2]. The essential function of the dielectric is to accumulate the charges generated from the plasma and limit the current, thus preventing the formation of spark and arc. This supports the generation of microdischarges, ultrafast discharge events lasting shorter than plasma thermalization time. The history, principles and applications of DBDs have been summarized and reviewed by U. Kogelshatz [3]. A particular application of volume, surface and coplanar DBD arises from the need of thick volume or thin surface plasma. Whereas volume DBDs are more favourable for the treatment of gases or particles of a wide range of diameters from nanopowders

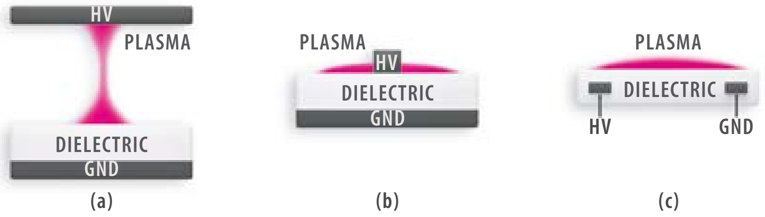

FIGURE 1: Dielectric barrier discharges of a) volume, b) surface and c) coplanar electrode configuration.

SUMMARY

The aim of the current paper is to introduce technology for the generation of high-power density surface plasma by a diffuse coplanar surface barrier discharge (DCSBD) plasma unit. The diffuse and uniform plasma generated in low-cost gases such as open air enables easy integration into novel or existing roll-to-roll (R2R) lines. We briefly discuss the history of the development of dielectric barrier discharges (DBDs) toward the most advanced plasma sources based on the coplanar arrangement of electrodes. Moreover, we present and discuss the advantages and disadvantages of the effect of volume and coplanar DBD treatments performed in R2R mode on the surface of polyamide. The paper also discusses the potential of R2R plasma treatments for next-generation applications of novel flexible and printed electronics.

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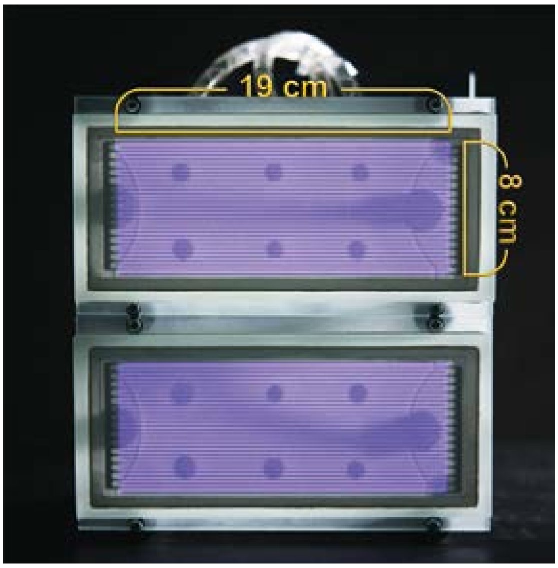

FIGURE 2: **Two flat DCSBD plasma units powered by RPS400 system operating simultaneously in the open air.**

to sub-mm plastic waste, surface and coplanar DBDs are more appropriate for the treatment of thermally sensitive surfaces. This is related to the orientation of streamers and ratio between diffuse and filamentary plasma. In volume DBD, the streamers and thus the energy flux in microdischarges is oriented from one electrode to the other and energy hitting the treated surface is strictly localized in small spots of tens-μm in diameter. For surfaces that are sensitive to heat, e.g., polypropylene non-wovens or other fabrics, it may lead to the unwanted effect called pinholing, i.e. damage of material surface in the form of tiny craters distributed on the surface. On the other hand, the streamers in the surface and coplanar DBDs are oriented parallel to the treated material, the ratio between filamentary and diffuse plasma is smaller and the energy density of the plasma is higher. Although surface and coplanar DBDs are not favourable for continuous treatment of gases, generation of ozone, etc., they provide a much higher efficiency in the treatment of surfaces, especially thermally sensitive plastic foils and mechanically delicate nanostructures.

In 2003, research groups supervised by Kando and Černák (Roplass s.r.o. founder and owner) reported the first use of surface DBD to modify non-woven polymer fabrics [4,5], and since then surface DBD has been used to modify polymeric materials many times. However, long-term usage (>100 hours) of surface DBD leads to erosion of the upper strip-like electrode, which negatively affects the overall lifetime and renders its use in industrial applications problematic [6,7]. Limited lifetime and low level of safety (the surface of a plasma unit cannot be touched by a naked hand due to a direct contact with high-voltage electrode) resulted in efforts to develop plasma units based on coplanar design. The concept was already known from plasma displays [8], but the total power delivered to plasma was extremely low. In 2002, a group led by Černák at Comenius University in Bratislava, Slovakia, constructed the first large-area coplanar DBD of power densities up to 100 W/cm^3 corresponding to 2.5 W/cm^2 [9]. Even though the areal power density of 2.5 W/cm^2 is similar to volume DBD, the spatial power density 100 W/cm^3 is one of the highest reported for diffuse plasma generated in the open air. The concept of coplanar DBD was later adopted by Masaryk University in Brno, Czech Republic, resulting in the foundation of its spin-off Roplass s.r.o. The coplanar plasma technology developed at Comenius University, advanced at Masaryk University and commercialized by Roplass Ltd. is often termed as *diffuse coplanar surface barrier discharge* (DCSBD). The latest photo of DCSBD in the open air is shown in **Fig. 2** and it can also operate in a wide range of pressures [10] and generate diffuse, homogeneous plasma at atmospheric pressure in other working gases as hydrogen, nitrogen, oxygen, argon, helium, carbon dioxide, methane, and others.

Recently, Štěpánová et al. investigated the difference between volume DBD and DCSBD, both mitigating a roll-to-roll setup, on the surface treatment of flexible polyamide (PA) foils [11]. **Fig. 3** shows the wettability measured by water contact angle methods, and its development for plasma-treated samples stored under open-air laboratory conditions. Apart from the higher wettability of PA foils after DCSBD treatment (at the same areal power density), the stability of the PA foils in the course of storage time was significantly higher after DCSBD treatment as well. The decrease in the wettability of plasma-treated polymers is related to the thermodynamically driven reorientation of hydrophilic polar groups towards the bulk. This effect can be hindered by the presence of a cross-linked surface which is mainly driven by diffuse plasma predominantly generated by surface DBD and DCSBD [11,12].

3 Advantages and peculiarities of coplanar DBD

The main advantage of generating surface plasma rather than volume plasma is in a more suitable orientation of microdischarges leading to a higher ratio of diffuse-to-filamentary plasma and thus resulting in a higher treatment efficiency of thermally sensitive materials. On the one hand, the

ZUSAMMENFASSUNG

Großflächige offene Plasmaquellen für Rolle-zu-Rolle-Fertigungsanlagen – Oberflächenplasmen hoher Leistungsdichte durch diffuse koplanare Oberflächenbarrierenentladungen

Ziel dieses Beitrags ist die Einführung einer Technologie zur Erzeugung eines Oberflächenplasmas mit hoher Leistungsdichte durch eine diffuse koplanare Oberflächenbarrierenentladung (DCSBD). Das diffuse und gleichmäßige Plasma, das in kostengünstigen Gasen wie z.B. an Luft erzeugt wird, ermöglicht eine einfache Integration in neue oder bestehende Rolle-zu-Rolle (R2R)-Anlagen. Wir erörtern kurz die Entwicklungsgeschichte der dielektrischen Barriereentladungen (DBDs) bis hin zu den modernsten, auf einer koplanaren Anordnung der Elektroden basierenden Plasmaquellen. Darüber hinaus werden die Vor- und Nachteile der Auswirkungen von Volumen- und koplanaren DBD-Behandlungen im R2R-Modus auf die Oberfläche von Polyamid vorgestellt und diskutiert. In dem Beitrag wird auch das Potenzial von R2R-Plasmabehandlungen für die nächste Generation von Anwendungen für innovative flexible und gedruckte Elektronik diskutiert.

generating plasma in a thin layer of approximately 0.2 – 0.3 mm has an advantage of a high spatial power density. On the other hand, the plasma in such a thin layer renders the treatment of nonporous flat surfaces problematic because plasma treatment is most efficient for distances between the plasma unit and the treated surface of approx. the same distance of 0.2 – 0.3 mm [13]. Especially for large-area flat materials, e.g. plates of soda-lime glass to be plasma-treated before application of a coating, it is technically challenging to maintain a precise distance over the entire area, and such an issue can significantly increase the cost of the line [14]. For an R2R line, which usually employs lightweight, flexible materials such as plastic foils, the plasma-treated surfaces of non-conductive materials result in a fast accumulation of charges on its surface, leading to the attraction of the plasma-treated material towards the plasma. As a result, plasma-treated material is directly attached to the plasma unit and the gas gap for the generation of plasma shrinks to zero. If the material is thin enough (hundreds of microns), plasma is generated on the top of the treated material as the plasma-treated material becomes part of the dielectric, and in this case, this material is sliding with one side over the plasma unit and is plasma-treated on the other. The sliding of the material over the DCSBD plasma unit was utilized in an R2R treatment of non-woven polypropylene fabric, which is porous and thin enough, so the plasma is generated in the entire volume of the fabric [15]. As a result of issues related to the treatment of non-conducive, nonporous, lightweight, flexible materials, a concavely curved DCSBD (diameter 14.8 cm) plasma unit of the same electrode and power supply parameters was developed. The curved plasma unit is attached to the roll, as shown in **Fig. 4**, and the flexible material stretched over the roll prevents the plasma-treated material from moving towards the plasma unit. Furthermore, the roll and the unit can be directly integrated into the existing R2R lines, and treatment width and efficiency can be upscaled using of multiple plasma units next to each other and in a row, respectively.

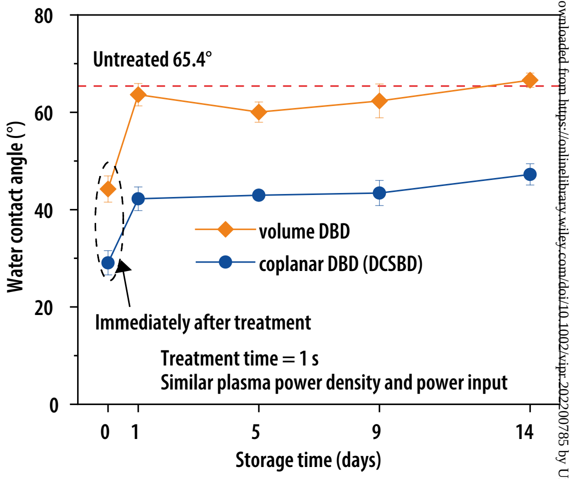

FIGURE 3: Water contact angle development on PA foil treated by volume DBD and DCSBD plasma and stored under open-air laboratory environment. Data reused from Štěpánová et al. (Figure 4 in original article) [11] , with Elsevier permission.

4 Roll-to-roll plasma setup and its applicability for inline manufacturing of flexible electronics

An example of a suitable use of R2R processes with DCSBD plasma is in thin-film optoelectronic applications based on metal oxide electrodes. Indium-tin oxide (ITO) is widely used in the semiconductor industry as well as in research as a transparent base electrode in solar cells (SCs) and organic light-emitting diodes. However, the surface of ITO (as well as fluorine-doped tin oxide, FTO) is sensitive to surface contaminants which can deteriorate its optoelectronic properties and thus the capability of good charge injection into subsequent layers. DCSBD plasma can provide rapid cleaning of ITO and FTO flexible surface in a few seconds and increase various optoelectronics parameters, including material work function (WF), which is directly related to the efficiency of charge injection. Fig. 5 shows the relation between the work function of plasma-treated ITO surfaces stored under open air in the laboratory and a dry nitrogen glove box for 35 days [16]. It was observed that plasma treatment of flexible ITO in an R2R mode for as short as 2 seconds led to an immediate increase of WF from 3.9 eV to >5 eV. The plasma-treated ITO was tested as a base electrode in n-i-p perovskite SC and the same power conversion efficiency was reached compared to SC constructed with ITO cleaned chemically, which took approximately 1 hour [17]. Indeed, chemical cleaning is not compatible with R2R, and next-generation R2R lines for optoelectronic applications require novel concepts based on cold plasma that can address rapid and efficient treatment without affecting the bulk properties of the plasma-treated materials. Furthermore, **Fig. 5** also shows that plasma-treated ITO surface is not stable, and WF has a tendency to recover, as was also observed for PA foils shown in **Fig. 3**. Here, the surface was stored under two distinct atmospheric conditions, laboratory air and nitrogen, however, both with considerably high amounts of hydrocarbons. ITO surfaces stored in the environment without oxygen and humidity show a slower decrease of WF towards its original value, and in both cases, stability at approx. 4.5 eV was reached after 35 days. This is important

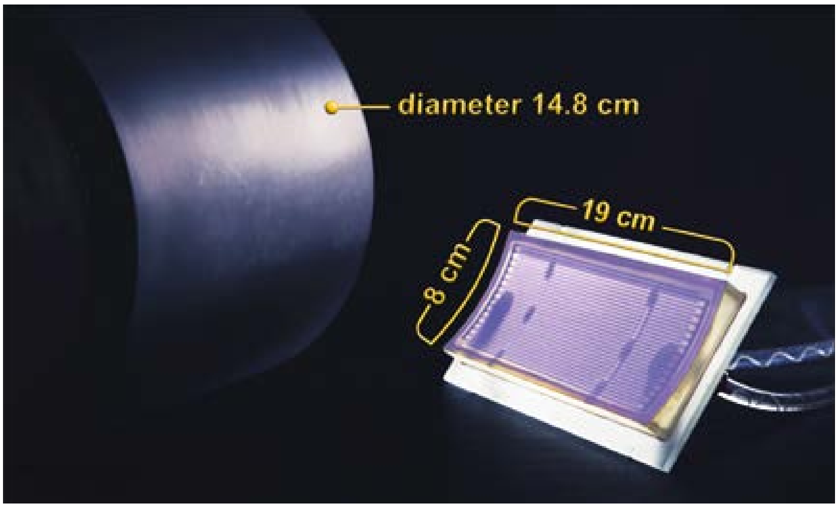

FIGURE 4: Concavely curved DCSBD plasma unit powered by RPS400 system for R2R (right) and a typical compatible rubber roll.

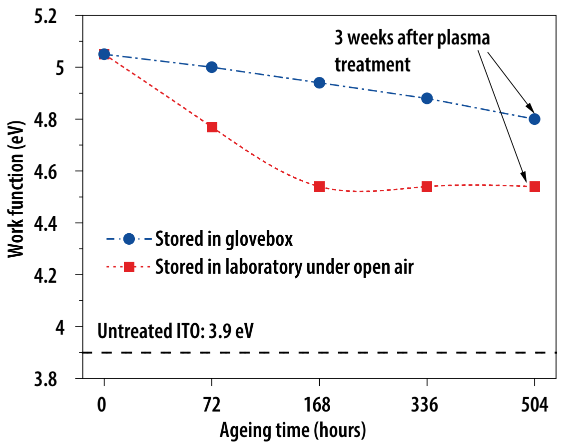

FIGURE 5: **Evolution of work function on 2-sec plasma-treated ITO surface with storage time under ambient air in laboratory and nitrogen glove box. Reproduced from Ref. [16], with Elsevier permission.**

for both PA polymer and ITO surfaces from R2R inline treatment perspective because the results show that plasma treatment does not necessarily have to be performed inline immediately before the coating step, and surfaces can be plasma processed remotely on one site, properly packed and transported to other R2R lines, while surface conditions are still convenient for the target application.

Conclusion

This contribution briefly summarizes aspects of open-air plasma technology based on diffuse coplanar surface barrier discharge and used in various commercially available plasma sources by Roplass s.r.o. Whereas flat DCSBD plasma units are suitable for rigid materials treated at a distance equal to approx. thickness (~ 0.3 mm) of plasma, treatment of porous materials, e.g. polypropylene non-woven fabrics, can be performed when treated fabrics slide over the flat plasma unit, while plasma is generated in the volume of the porous fabrics. Issues related to electrostatic attraction of lightweight material towards plasma units led to the development of concavely curved DCSBD plasma units and their direct employment into R2R lines for the treatment of flexible materials. DCSBD plasma generated under open-air is capable of swift and profound changes on various surfaces, such as in the case of polymers (thermoplastics) by incorporating polar groups responsible for the hydrophilic surface treatment or of metal-oxide transparent electrodes by means of a rapid cleaning of hydrocarbons from its surface. In terms of energy efficiency, DCSBD operates at low energy doses sufficient enough to induce changes on the treated surface and under low-cost ambient air. Compared to other competitive R2R-compatible plasma technologies, e.g. volume DBD (often termed as industrial corona), DCSBD produces a considerably higher volume of diffuse plasma, which is beneficial for a higher stability of plasma-treated polymers and provides a milder treatment without any unwanted pinholing or other damage of the substrate. Compared to plasma jets, which are sources of well-defined plasma localized in tiny (approx. 1 mm^2) spots, DCSBD provides a considerably higher areal treatment and relatively easy upscaling.

DCSBD is a robust and mature technology generating a uniform thin layer of high-power density plasma without any hazard arising from the transition towards spark and arc. It can be applied in rapid surface treatment of a wide-range of various materials, e.g., non-conductive, semi-conductive and fully-conductive materials of any thickness, flexibility and length. The potential to deploy DCSBD into R2R designates it for the manufacture of next-generation applications in flexible and printed electronics.

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