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The barrier discharge: basic properties and applications to surface treatment

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Abstract

Barrier discharges (BDs) produce highly non-equilibrium plasmas in a controllable way at atmospheric pressure, and at moderate gas temperature. They provide the effective generation of atoms, radicals and excited species by energetic electrons. In the case of operation in noble gases (or noble gas/halogen gas mixtures), they are sources of an intensive UV and VUV excimer radiation. There are two different modes of BDs. Generally they are operated in the filamentary one. Under special conditions, a diffuse mode can be generated. Their physical properties are discussed, and the main electric parameters, necessary for the controlled BD operation, are listed. Recent results on spatially and temporally resolved spectroscopic investigations by cross-correlation technique are presented. BDs are applied for a long time in the wide field of plasma treatment and layer deposition. An overview on these applications is given. Selected representative examples are outlined in more detail. In particular, the surface treatment by filamentary and diffuse BDs, and the VUV catalyzed deposition of metallic layers are discussed. BDs have a great flexibility with respect to their geometrical shape, working gas mixture and operation parameters. Generally, the scaling-up to large dimensions is of no problem. The possibility to treat or coat surfaces at low gas temperature and pressures close to atmospheric once is an important advantage for their application.

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1. Introduction

Dielectric barrier discharges, also referred to as barrier discharges (BD) or silent discharges are

plasmas far from equilibrium [1,2]. Besides the ozone synthesis, the scope of their applications covers incoherent ultraviolet (UV) or vacuum ultraviolet (VUV) excimer radiation in excimer lamps, the generation of highly intensive coherent radiation in CO₂ lasers, flat plasma displays of large dimensions as well as various applications in the field of environmental protection (pollution

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control, destruction of hazardous compounds), surface treatment (modification, cleaning, etching) and layer deposition [3–11]. The treatment of surfaces has already a long tradition [4–8]. This technique, misleadingly called as “corona treatment,” is used, e.g. to promote the wettability, printability and adhesion on polymer surfaces. The surface treatment of dielectric as well as of conducting materials is possible. Recent activities focus on the deposition of thin films—a field traditionally dominated by low pressure plasma processing [9–13].

Decisive advantage of the BDs for the wide field of applications are the non-thermal plasma conditions at low gas temperatures and at elevated (typically atmospheric) pressure. BDs provide high-energy electrons which are able to generate atoms, radicals and excited particles. These discharges demonstrate a great flexibility with respect to their geometrical shape, working gas mixture composition and operation parameters (e.g. power input, frequency of feeding voltage, pressure, gas flow) [1,2]. In many cases, when these parameters have been optimized before in small laboratory devices, there are no problems in scaling up the conditions to larger (industrial) dimensions. Usually, the BD operates in the so-called filamentary mode. Under (very) special conditions of the operation, there exist a diffuse (glow) mode, too. In the latter case, referred to as atmospheric pressure glow discharge (APGD), the BDs are very suitable for a uniform surface treatment [14–20].

The generation of reactive particles (atoms, radicals, excited species, ions) and of radiation at short wavelength for surface treatment is controlled by the plasma parameters of the BD, mainly by the reduced local electric field strength and by the electron density. Their knowledge is of essential importance for the desired control of the plasma processes. Experimental and theoretical studies of BDs in the filamentary mode have a long history [1,2,21–28]. However, despite of considerable progress in understanding the structure and properties of these discharges, that was made mostly during the last few decades, the knowledge of this subject nowadays appears to be insufficient to provide an adequate quantitative theoretical description for the BD behavior. Main reasons for

this situation are the difficulties to investigate experimentally the dynamics of the discharge filaments, requiring a sub-ns temporally and sub-mm spatially resolution. Recently, many efforts have been put forth to understand in detail the establishment of the diffuse mode on the level of elementary processes, too [18,29,30,31].

In the present paper, an overview on the basic properties of BDs is given. The most important electrical parameters which control the operation of BDs have been summarized together with the description of the minimum technical equipment required for their measurement. Recent results on experimental investigations on the filament dynamics are presented, which have been obtained by the technique of cross-correlation spectroscopy (CCS) [32,33]. These experiments enable the estimation of local plasma parameters for a BD in the filamentary form. Conditions to generate the glow mode of BDs are discussed for selected operating media. Furthermore, a general overview on the application of BDs to surface treatment and layer deposition is presented. Selected examples are outlined in more detail to show the influence of the BD properties on surface processes. Therefore, the paper has not the aim to review all fields of surface treatment by BDs. In particular, results on the comparison of the polymer treatment by filamentary and diffuse (glow) form of BDs and the VUV catalyzed deposition of metallic layers based on the BD generated excimer radiation are discussed.

2. Physical properties of barrier discharges

2.1. Atmospheric pressure plasmas and configurations of barrier discharge

Atmospheric pressure plasmas are subdivided into non-thermal and thermal ones. The corresponding conditions are illustrated in the Fig. 1. Examples for plasma sources important for numerous applications are listed, too. The conditions of non-thermal plasmas are mainly characterized by a relatively low temperature of the neutral gas in contrast to a significantly higher kinetic temperature of the electrons. The

non-equilibrium between these main components is permanently maintained by applying DC or AC electric fields to the discharge electrodes. The gas temperature is often near room temperature. Therefore, these plasmas are named low-temperature non-equilibrium plasmas, too. BDs belong to this group besides, e.g. corona discharges, micro hollow cathode discharges and so-called one atmosphere uniform glow discharge plasmas (OAUGDP, re-invented in 1995 [34]). In thermal

plasmas, all species have an identical temperature characterized by one Maxwellian velocity distribution function of particles. Consequently, they are in the complete (or at least local) thermal equilibrium which can be reached only sufficiently far from solids in contact with plasmas. This group includes, e.g. arcs and inductively coupled plasma torches. Microwave plasma sources can provide both regimes, depending on the operation conditions.

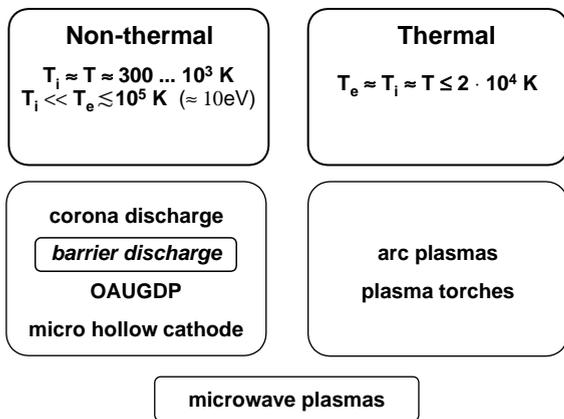


Fig. 1. Subdivision of plasmas at atmospheric pressure (OAUGDP: One atmosphere uniform glow discharge plasma [34]).

Typical electrode arrangements of planar and cylindrical BDs are shown in Fig. 2. The presence of one or more dielectric layers in the current path between the metallic electrodes through the discharge gap is essential for the discharge operation. Typical materials for dielectric barriers are glass, quartz and ceramics. Plastic foils, teflon plates and other insulating materials can be used, too. There are many excellent monographs and papers on the physics of BDs, e.g. [1,2,27,28,35]. Here the most important characteristics of discharge operation are summarized. Because of a capacitive coupling of the insulating material to the gas gap BDs can be driven by alternating feeding voltage and by pulsed DC voltages as well. When a high enough voltage is applied an electrical breakdown occurs. Typical operation conditions of BDs in air are listed in Table 1.

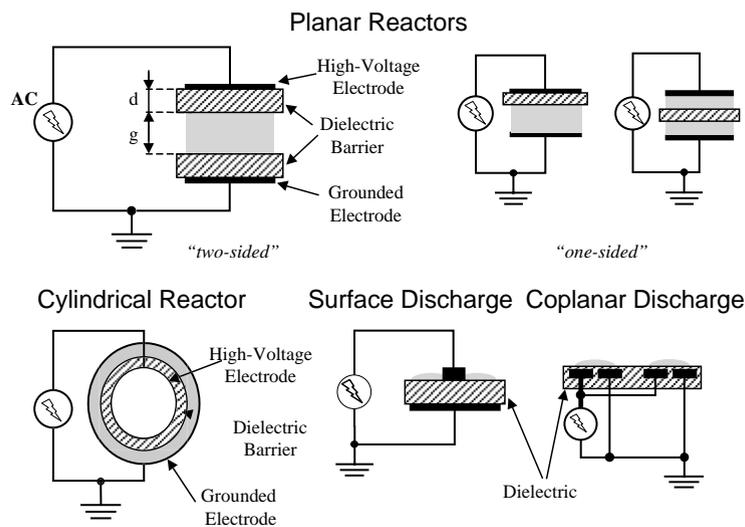


Fig. 2. Typical electrode arrangements of barrier discharges.

Table 1
Typical operation conditions of barrier discharges in air [1,2]

| | |
|--|--|
| Electric field strength E of first breakdown | $\cong 150 \text{ Td}$ ($p = 1 \text{ bar}$, $T = 300 \text{ K}$) |
| Voltage V_{pp} | 3–20 kV |
| Repetition frequency f | 50 Hz–10 kHz |
| Pressure p | 1–3 bar |
| Gap distance g | 0.2–5 mm |
| Dielectric material | glass, Al_2O_3 , ferroelectrics, ... |
| Thickness d | 0.5–2 mm |
| Relative dielectric permittivity ϵ_r | 5–10 (glass), ..., 7000 (ferroelectrics) |

2.2. Filamentary barrier discharge

2.2.1. Electrical parameters

Usually the BD operates in the so-called filamentary mode. If the local electric field strength in the gas gap arrives the ignition level, the breakdown starts at many points followed by the development of filaments, named microdischarges [1,2,22–28,35] (compare chapter 2.2.2). The microdischarges are of nanosecond duration, uniformly distributed over the dielectric surface. To characterize the overall discharge behavior, an equivalent electric circuit can be used. An example of such a circuit is shown in Fig. 3 for the simplest case of one dielectric barrier, only. As long as the gap voltage U_g is smaller than the ignition voltage, there is no discharge activity and the device behaves like a series combination of two capacitances: the gap capacitance C_g and the capacitance of dielectric C_d (compare Fig. 3). Then the total capacitance C is given by the expression

$$C = \frac{C_d C_g}{C_d + C_g} = \frac{C_g}{1 + C_g/C_d} = \frac{C_g}{1 + d/(\epsilon_r g)}. \quad (1)$$

Since typically $\epsilon_r = 5–10$ (glass dielectrics) and $g \approx d$ (compare Table 1), the term $C_g/C_d = d/(\epsilon_r g) \approx U_d/U_g \ll 1$ (U_d : voltage across dielectric barrier). Therefore, the total capacitance C is controlled by the capacitance of the gas gap C_g . The gap voltage U_g is close to the feeding voltage $U(t)$. If U_g overcomes the ignition voltage microdischarges are initiated. During this active phase [$t_1 \dots t_2$] within every half cycle, the discharge voltage U_D remains approximately constant, $U_g = U_D \approx \text{const}$, although the current flow through discharge gap is maintained by a large number of microdischarges. The discharge voltage U_D mainly

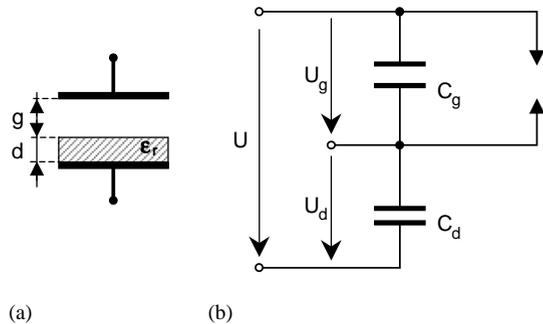


Fig. 3. One-sided BD configuration (a) and the equivalent circuit (b).

depends on the gas composition, pressure and gap spacing.

The important electric operation parameters of BDs, in particular the above-discussed discharge voltage U_D , discharge current $I(t)$, transferred charge Q , electric power input P_{el} (consumed electric energy E_{el} , respectively), averaged reduced field strength E/p , can be estimated by the setup given in Fig. 5. The BD, denoted as capacitance C , is fed by an alternating voltage $U(t)$. The current pulse shape $I(t)$ and the $(Q - U)$ charge-voltage-characteristic can be registered alternatively using either a resistance R_{meas} ($R_{meas} \approx 50 \Omega$) or a capacitance C_{meas} ($C_{meas} \approx 10 \text{ nF}$) by means of an oscilloscope. The measurement of the high voltage requires the transformation by a high voltage probe.

A typical oscillographic presentation of the discharge current, registered in air for sinusoidal feeding voltage $U(t)$ is shown in Fig. 6. Every current pulse corresponds to a series of microdischarges as already illustrated schematically in Fig. 4. An example of idealized $Q-U$ -diagram is

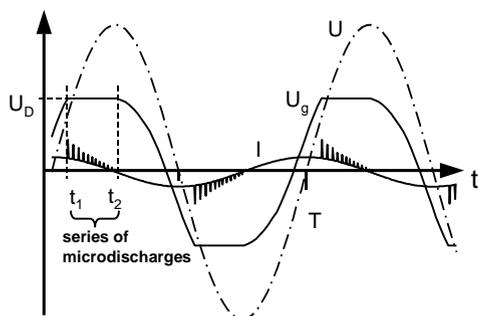


Fig. 4. Schematic picture of the feeding voltage $U(t)$ and discharge current $I(t)$.

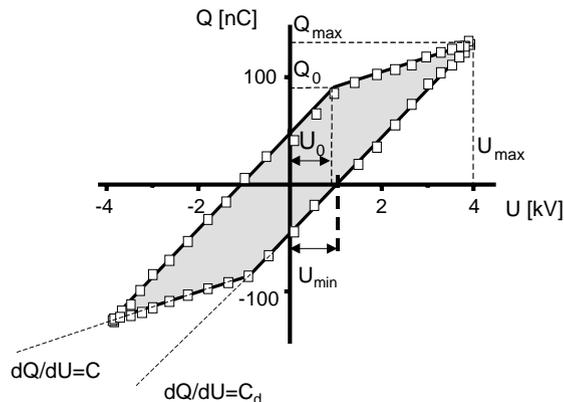


Fig. 7. An $Q-U$ -oscillographic presentation (Lissajous figure).

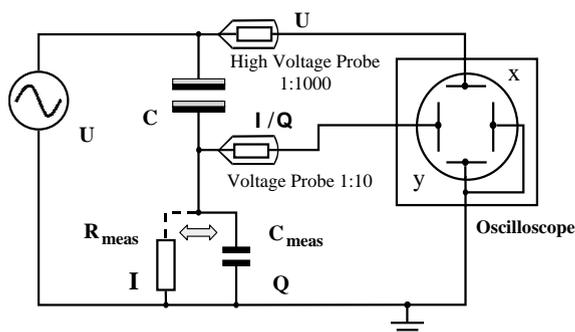


Fig. 5. Experimental setup for voltage, current and charge transfer measurements alternatively: either current measurement (using only R_{meas} ; broken line) or charge transfer measurement (using only C_{meas} ; as plotted).

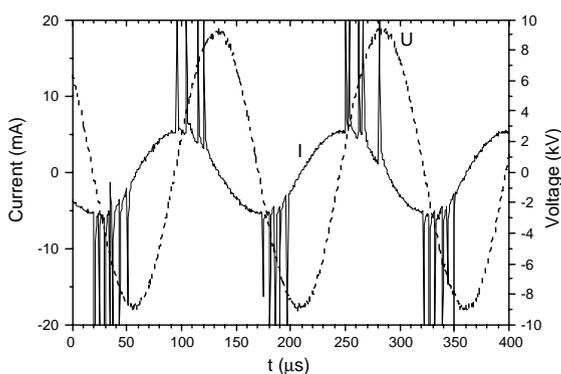


Fig. 6. Measurement of the voltage and current shape of the filamentary BD in air.

given in Fig. 7. From this so-called Lissajous figure the minimum external voltage U_{min} at which the ignition occurs (marked), the electric energy

consumed per voltage cycle E_{el} and the electric power P_{el} can be estimated by the following relations that have been derived and discussed in detail in [1–3]:

$$\begin{aligned}
 E_{el} &= \oint U(t) dQ = C_{meas} \oint U(t) dU_{meas} \\
 &= 4C_d \frac{1}{1 + C_g/C_d} U_{min}(U_{max} - U_{min}) \\
 &= 2(U_{max}Q_0 - Q_{max}U_0) \equiv \text{AREA of } (Q - U) \text{ diagram}
 \end{aligned}$$

$$P_{el} = \frac{1}{T} E_{el} = f E_{el}, \tag{2}$$

where f is the frequency of feeding voltage.

The discharge voltage U_D is close to the measured voltage U_{min} . It can be calculated by

$$U_D = U_{min} \frac{1}{1 + C_g/C_d}. \tag{3}$$

An estimation of the spatially and temporally averaged reduced electric field strength $\langle E/p \rangle$ follows from

$$\langle E/p \rangle = U_D/(gp). \tag{4}$$

The number of microdischarge series per half cycle $N_{T/2}$ can be derived under the assumption that all series transfer an identical charge ΔQ by

$$N_{T/2} \approx \frac{2C_d}{\Delta Q} (U_{max} - U_{min}). \tag{5}$$

If all microdischarges of one series (causing a single current pulse) have nearly identical properties, then $\Delta Q \approx nq$, where n is the number of microdischarges in a series and q is the charge transferred by one single microdischarge. This charge transfer is mainly determined by the sort of dielectric and the width of gas gap, and it is only weakly dependent on the gas pressure as well as on the thickness of the barrier. It means

$$q \propto \varepsilon_r g. \quad (6)$$

These relations have been validated by numerous experiments.

2.2.2. Microscopic behavior of filamentary barrier discharge

2.2.2.1. *Discharge structure.* The electrical breakdown of the gas gap in a BD starts almost simultaneously at many points of the surface and proceeds via the development of microdischarges. Their development can be sub-divided into three steps [1,2,27,32,35]:

- (1) The pre-breakdown phase. A negative space charge of electrons (and negative ions due to attachment) is accumulated in front of the anode (according to the polarity of the half-cycle of applied voltage). The pre-breakdown phase lasts for at least $0.5 \mu\text{s}$. Finally, a high local electric field strength is created in front of the anode. If it reaches a certain critical level, the breakdown starts from the anode surface.
- (2) The propagation phase. It is governed by an ionization wave (i.e. a wave of high local electric field strength) in the direction to the cathode. On its way pairs of ions and electrons are produced. This phase takes typically 1–2 ns.
- (3) The decay phase. It is characterized by the charge accumulation on the dielectric surface compensating the external electric field. It is a period of decay of the light and current pulses of the microdischarges.

In the next half-cycle of the applied voltage, the microdischarge formation inversely renews. The dielectric barrier limits the amount of the transferred charge and energy deposited in a micro-

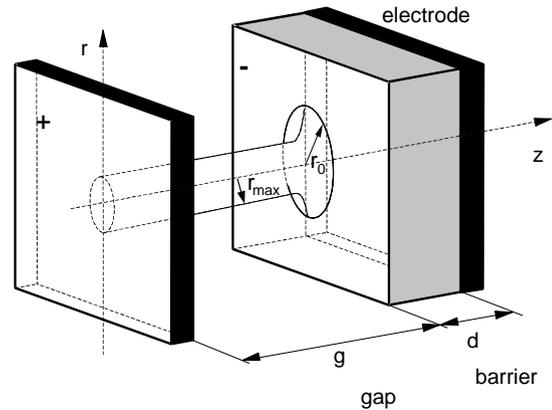


Fig. 8. The shape of a single microdischarge (r_{max} : radius of the filament, r_0 : radius of the footprint).

discharge channel. At the dielectric surface the microdischarge channels continue as surface discharges covering a much larger area than the diameter of the filament. The typical shape of a microdischarge channel is schematically shown in Fig. 8. The Figs. 9a, b demonstrate the footprints of the individual microdischarges left on the emulsion of photographic plates acting together with glass plates as dielectric surfaces. These footprints are called Lichtenberg figures. Characteristic properties of the microdischarges in air at atmospheric pressure are summarized in Table 2.

2.2.2.2. *Experimental investigation of microdischarge dynamics.* The time constants of the relevant processes in BDs cover many orders of magnitude. This situation is illustrated in Fig. 10. The development of microdischarge channels, which is characterized by the production of high-energy plasma electrons, takes place in the ns range. Otherwise, the phase of plasma chemical reactions by atoms, radicals, excited species and short waved radiation typically starts within the μs scale. Their production is controlled by the plasma parameters of the microdischarges, namely by the reduced local electric field strength and electron density. Therefore, the knowledge of these parameters is of essential importance for the desired control of the final plasma process.

The experimental investigation of the dynamics of microdischarge development and the measurement of plasma parameters requires a sub-ns temporal and sub-mm spatial resolution. Thus, it is not surprising that a great deal of effort has been devoted to computer simulation [1,2,22–27]. Regards experimental findings, the following important milestones should be mentioned: 1972—

identification of the separate microdischarges [37]; 1980—streak-photography of the single microdischarge [38,39]; 1983—accurate measurement of the microdischarge current pulses [40]; 1995—determination of the spectrally resolved spatio-temporal distributions of the microdischarge luminosity by means of the CCS [41,42]. 2001—spatially and temporally resolved quantitative estimation of local reduced field strength and relative concentration of electrons in air by CCS [32,33].

The main idea of the technique of CCS is to replace a direct measurement of the single pulse luminosity of a repetitive light pulse emitter by a statistically averaged determination of the correlation function between two optical signals, both originating from the same source. The first one of these signals (so-called “synchronizing signal”) is used to define a relative time scale, the second one (“main signal”) has to be detected with a probability at least one order of magnitude lower, than

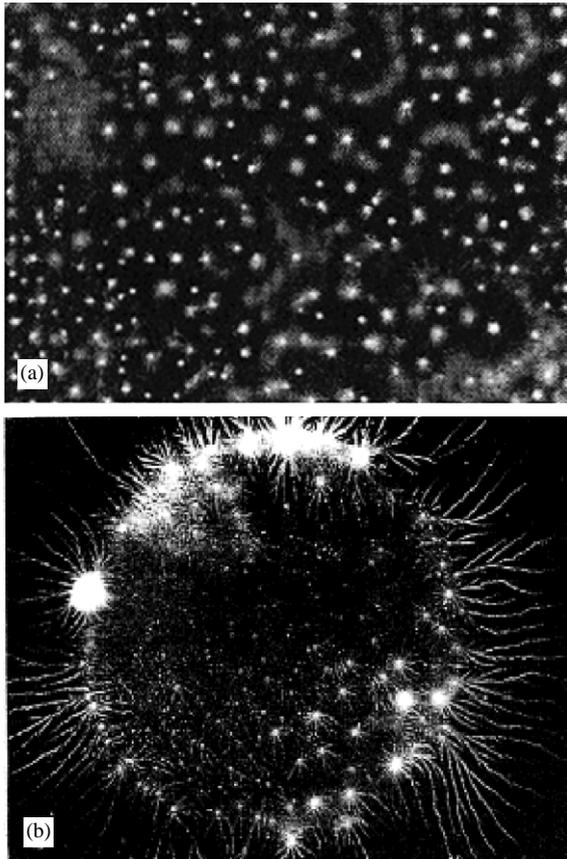


Fig. 9. Lichtenberg figures for the BD in (a) Xe [1] and (b) air (single +15 kV pulse [36]).

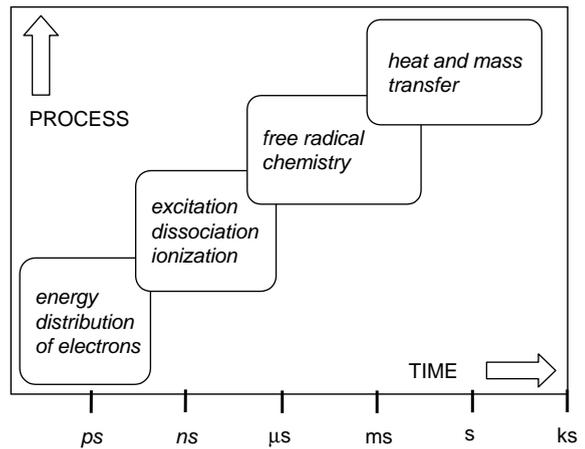


Fig. 10. Time scale of the relevant processes of the filamentary barrier discharge.

Table 2

Characteristic properties of a microdischarge channel in air at atmospheric pressure [1]

| | |
|---|--|
| Duration: a few nanoseconds | Total transferred charge: 10^{-10} – 10^{-9} C |
| Radius of filament: about 0.1 mm | Density of electrons: 10^{14} – 10^{15} cm ⁻³ |
| Peak current: 0.1 A | Mean energy of electrons: 1–10 eV |
| Current density: 10^6 – 10^7 A/m ² | Gas temperature of microdischarge: near room |

that one of the synchronizing signal. The measured quantity is actually a time delay between these two signals, and the recorded quantity is a probability density function for the light pulse intensity evolution. A general scheme of the experimental setup and measurement procedure is presented in Fig. 11. A single microdischarge BD, periodically generated at a defined position has been used as an emitter of repetitive light pulses. The localization could be realized by a special electrode arrangement (see Fig. 12). One more advantage of such a geometry of the discharge cell is the possibility to observe not only the volume part of the BD, but the surface discharges as well, provided that the range of axial scanning exceeds the gap width. Spatial resolution and scanning over the microdischarge axis was provided by the optical system shown in the left upper part of the figure. Monochromatic light of the main signal was detected by highly sensitive photo-multipliers.

The main characteristics of our CCS measurements are summarized in Table 3. More details on this technique are given in [32,33].

In Fig. 13, an example of the temporally and spatially resolved development of microdischarges in synthetic air for the $N_2(C^3\Pi_u)_{v''=0} \rightarrow N_2(B^3\Pi_g)_{v''=0}$ transition of the second positive system and the $N_2^+(B^2\Sigma_u^+)_{v''=0} \rightarrow N_2(X^2\Sigma_u^+)_{v''=0}$ transition of the first negative system of nitrogen is shown, also covering the pre-breakdown phase as well as the afterglow phase. These selected transitions correspond to extremely different excitation energies of the nitrogen molecule ($\Delta E = 11$ eV) and N_2^+ ion ($\Delta E = 19$ eV), respectively. These measurements are the basis for the derivation of the electric field strength in air at atmospheric pressure as proposed recently in [43–45]. The used kinetic model and details of the calculation are given in [32,33]. The spatially and temporally resolved values of reduced electric field

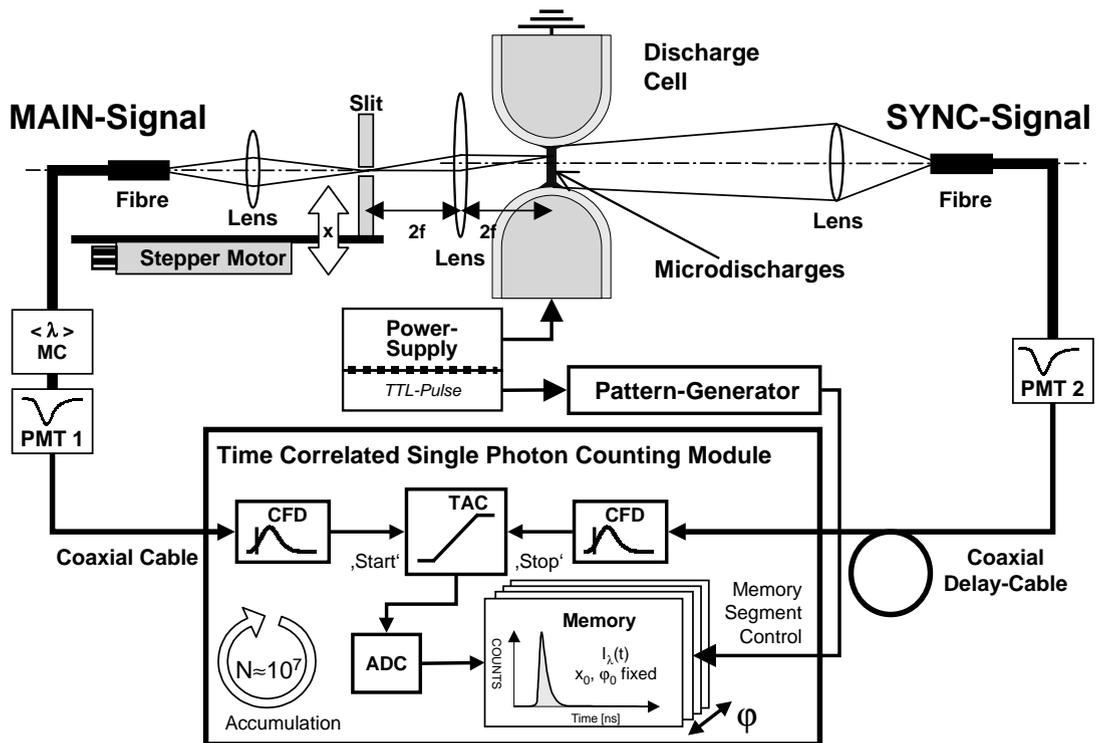


Fig. 11. A general diagram of the apparatus and measurement procedure. Abbreviations: SYNC—Synchronizing; MC—Monochromator; PMT—Photo-multiplier; TTL—Transistor–Transistor Logic; CFD—Constant fraction discriminator; TAC—Time-to-amplitude converter; ADC—Analogue-to-digital converter; φ is a phase of the feeding sinusoidal voltage (see Fig. 12).

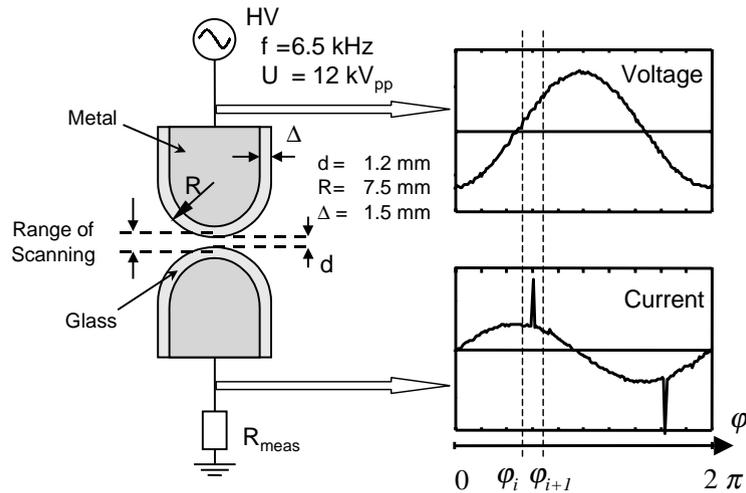


Fig. 12. Electrode arrangement with the indicated range of axial scanning, and a typical example of the oscillograms of voltage and current.

Table 3
Resolution parameters of the CCS measurements [32]

| Quantity | Resolution |
|--------------------------|---------------------|
| Time (50 ns scale) | <0.15 ns |
| Space (axial direction) | 0.1 mm |
| Wavelength | 0.3 nm |
| Phase of feeding voltage | $\varphi = 2\pi/16$ |

strength as well as the relative density of electrons for the conditions of Fig. 13 are summarized in Fig. 14.

In accordance with the in chapter 2.2.2.1 given qualitative characterization of microdischarge development, it propagates within 1–2 ns from the surface of the anode to the cathode as an ionization wave (=range of maximum local electric field strength), followed by a dark phase (=low electric field strength/low energy of electrons, respectively). After that a further intensive “glow” of the second positive system appears near the anode, indicating excitation processes by electrons of large density but low energy. The highest intensity of the first negative system has been observed at the cathode. It corresponds to the region of the highest electric field strength (and electron energy, respectively).

2.3. Diffuse (glow) barrier discharges

2.3.1. Phenomenology and electric characterization

Under certain operating conditions, a diffuse (glow) mode of BD can be obtained. Obviously, diffuse BDs are especially suitable for a uniform surface treatment. Important stages in the investigation of this discharge mode are listed in the following. Donohoe investigated in 1976 a uniform glow discharge with pulsed excitation in helium/ethylene mixtures [46]. Okazaki and co-workers in 1987 (and afterwards) operated barrier glow discharges even at 50 Hz sinusoidal feeding voltage, using an electrode configuration of two metal foils covered with a special metal mesh and ceramic dielectrics in helium, nitrogen (and even in air, oxygen and argon) with and without certain organic admixtures [14,15,47]. They proposed the term APGD; Massines and co-workers in 1992 (and afterwards) investigated in detail barrier glow discharges in helium and nitrogen [18,20,48]. This group contributed essentially to a better understanding of the existence of the glow mode in the studied systems on the level of elementary processes. Recent activities of several teams are focused on spatially and temporally resolved spectroscopic measurements ([49–51]) as well as on the development of theoretical models

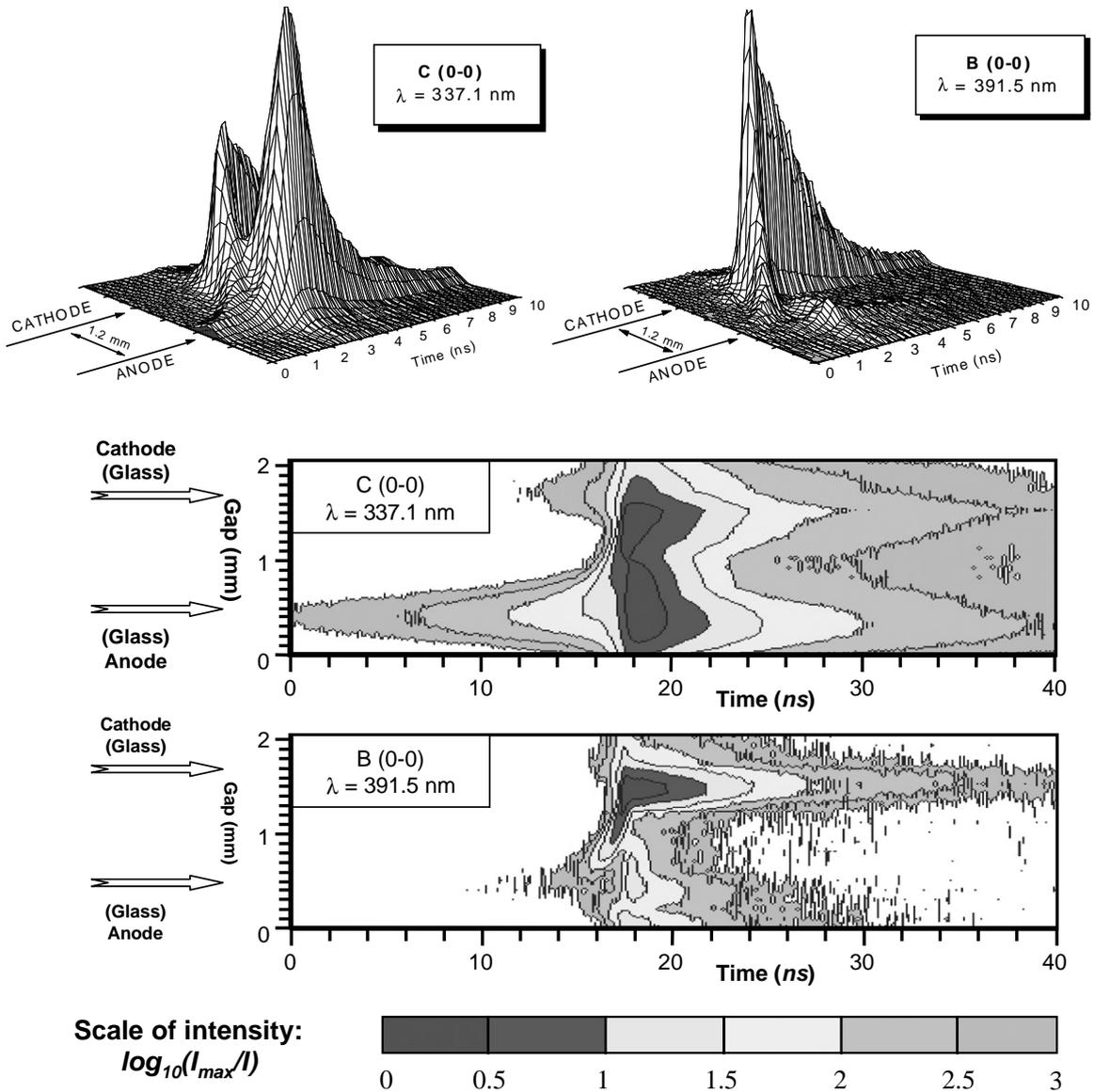


Fig. 13. Spatially and temporally resolved spectral intensities of the $N_2(C^3\Pi_u)_{v''=0} \rightarrow N_2(B^3\Pi_g)_{v''=0}$ transition of the second positive system and the $N_2^+(B^2\Sigma_u^+)_{v''=0} \rightarrow N_2^+(X^2\Sigma_u^+)_{v''=0}$ transition of the first negative system of nitrogen (conditions: synthetic air, $p = 1$ bar, flow = 100 cm, $V_{pp} = 13$ kV, $f = 6.5$ kHz, $g = 1.2$ mm, glass dielectrics, comp. Fig. 12).

[29,30,52]. Independently of these activities, Roth and co-workers re-invented in 1995 a uniform glow discharge in different gases at atmospheric pressure, named OAUGDP [34].

The generation of stable diffuse BDs at atmospheric pressure requires special operation conditions, that are mainly determined by the properties

of feeding gas. One important point seems to be an occurrence of effective pre-ionization, Penning ionization via metastables and primary ionization at low electric field, as compared to the conditions of the BDs in the filamentary mode. Of course, the diffuse BD mode is sensitive to impurities, admixtures, metastables and residual ions. The

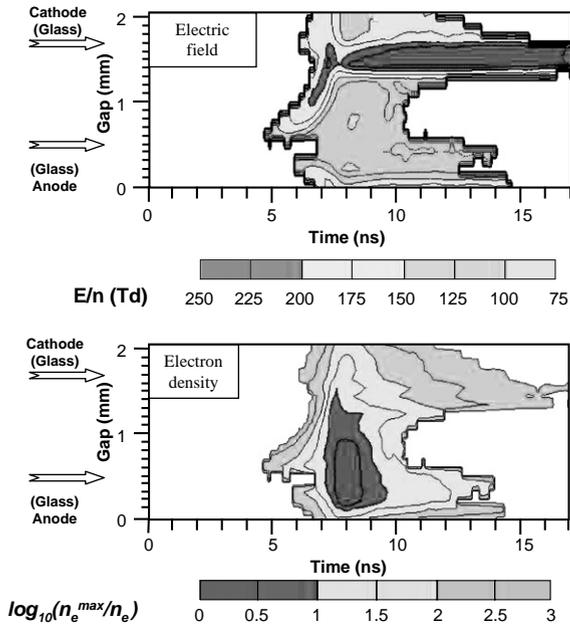


Fig. 14. Spatially and temporally resolved local reduced field strength and relative electron density of the single micro-discharge in synthetic air (conditions of Fig. 13).

densities of residual species from the previous half-period that can initiate the diffuse discharge generation in the next half-cycle, are dependent on the repetition frequency. Therefore, the feeding voltage frequency plays an important role in the transition to the diffuse mode. Some dielectric materials (e.g. electrets) can trap appreciable amounts of charges uniformly on the surface. When the electric field changes its polarity, the charge carriers are expelled from the surface initiating a diffuse discharge development [19]. The required operation conditions can be easily established in helium, neon and pure nitrogen. For the case of nitrogen the discharge mechanism is discussed below in more detail.

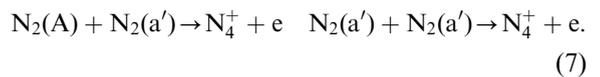
The electric equivalent circuit (see Fig. 3) as well as the experimental setup (see Fig. 5) for the electric characterization of the filamentary BD can be used for the diffuse BD as well. Examples of the oscillograms of $I(t)$ for a sinusoidal feeding voltage $U(t)$ in nitrogen and helium are shown in Fig. 15a, c. Contrary to the filamentary mode (compare Fig. 6), the current curves have a smooth

shape. There are two components forming the total current in the outer circuit: the displacement current driven through the dielectric material and the net discharge current (compare the details in Fig. 15a). Whereby the single current pulse of the filamentary BD lasts for some nanoseconds, the time scale for diffuse BD is determined by the frequency of feeding voltage. At the frequencies of some kHz, the ms ... μ s scale is relevant.

2.3.2. On the discharge mechanism

Much effort has been put forth to understand the mechanism of the formation of diffuse BDs, as outlined above. Despite considerable progress in this field in the last years, there are still many open questions. The basic mechanisms are strongly affected by the properties of the feeding gas. This can be illustrated by the comparison of the BDs in helium and nitrogen. In Fig. 15b,d spatially and temporally resolved intensity distributions of intensive lines from helium and nitrogen are shown. They were obtained by means of the modified setup presented in Fig. 11. The maximum glow intensities of nitrogen and helium are located at the opposite electrodes, indicating to the quite different dominant ionization and excitation mechanisms for both gases. In helium effective ionization and excitation processes occur in the electric field of the cathode region by direct collisions of atoms with energetic electrons and by three body processes, generating He^+ and He_2^+ ions (glow mode) [18,31,52]. Penning ionization processes via nitrogen impurities in He seems to be important, too [52].

On the contrary, in nitrogen there must be another mechanism of the effective production of ions and electrons. On the one hand, kinetic models of diffuse BD in nitrogen come to the conclusion that Penning ionization by two-body collisions of metastable nitrogen molecules producing N_4^+ ions and electrons are very important [29]:



On the other hand, recent simulations have shown that surface electrons must be considered in the current balance for efficient primary ionization

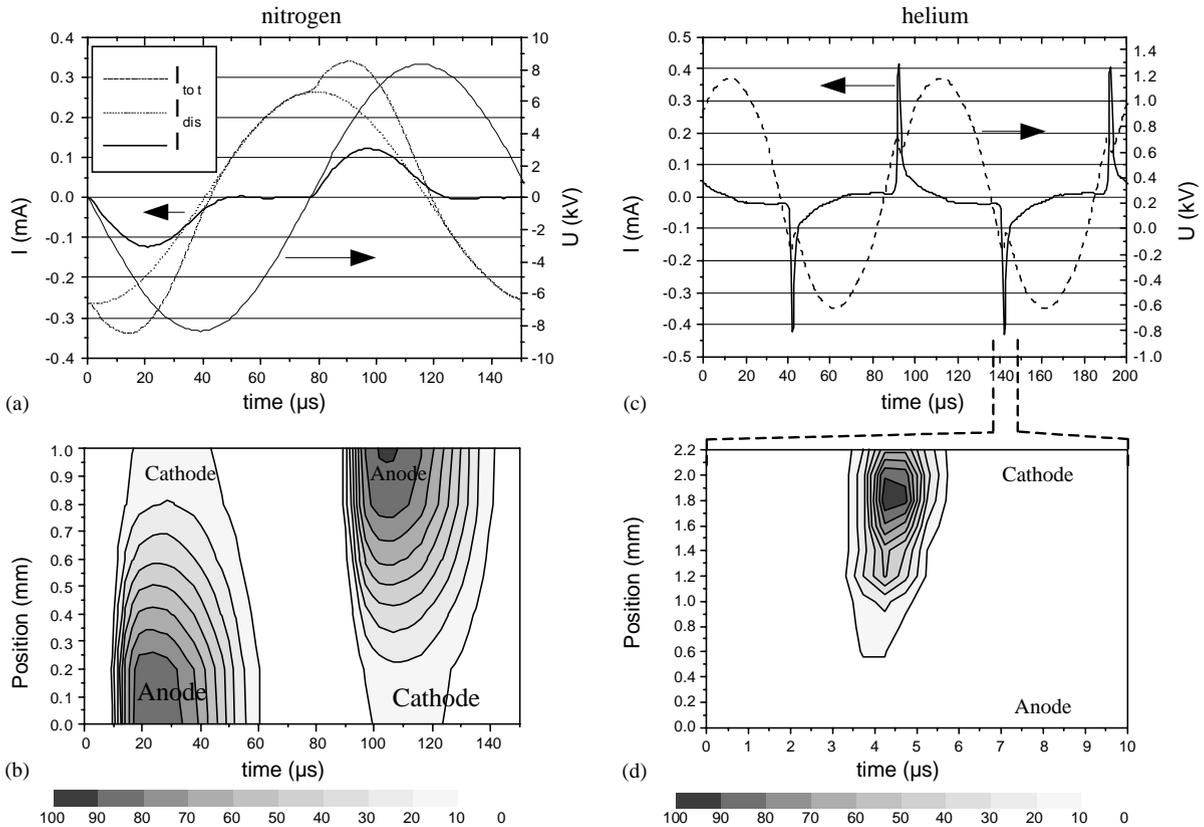


Fig. 15. $U(t)$ - and $I(t)$ -dependencies of diffuse barrier discharges in nitrogen and helium, and the corresponding spatio-temporally resolved emission intensities (conditions in He: $\lambda = 706$ nm of HeI, $p = 1$ bar, flow = 1000 sccm, $f = 10$ kHz, $V_{pp} = 2.4$ kV, $g = 2.2$ mm; conditions in N_2 : $\lambda = 337$ nm of the $\text{N}_2(\text{C}) \rightarrow \text{N}_2(\text{B})$ transition, $p = 1$ bar, flow = 700 sccm, $f = 6.5$ kHz, $V_{pp} = 18$ kV, $g = 1$ mm; I_{total} : total current; I_{dis} : displacement current; I : discharge current).

processes at low electric field strength, coming into the volume when the electric field changes its polarity [30]. Metastable molecules as well as $\text{N}_2(\text{C})$ molecules are effectively generated by electron collisions. Their local density has its maximum in the anode region. This behavior is in agreement with the detected intensity distributions. In the mixtures of nitrogen and oxygen (e.g. in air), the metastable molecules are quenched very effectively by molecular oxygen, reducing drastically the densities of metastables. Therefore, in dry air (already in nitrogen with an admixture of about 500 ppm oxygen [49]), the direct ionization of nitrogen molecules in the ground state by electrons is dominant. This process requires

electrons with energies $E \geq 18.7$ eV, i.e. a comparatively high local field strength. However, under the conditions of effective collisional quenching of nitrogen metastables, there is no other way of discharge development. That is an important reason for the transition to the filamentary BD (compare chapter 2.2.2).

2.4. Some conclusions with respect to surface treatment

The properties of the microdischarges of filamentary BDs do not depend on the external driving circuit (e.g. the frequency, feeding voltage wave form) over a wide range of operation

conditions. They are mainly controlled by the feeding gas mixture composition. For example, a growth of the power density for a given discharge configuration results in an increase in the number of microdischarges per unit of surface area and/or per unit of time. This fact is very important for the scaling-up of BD configurations to industrial dimensions.

With respect to a uniform surface treatment, diffuse discharge conditions are very desirable. But, there are only small windows of their existence (compare chapter 2.3). Otherwise, under the operation in the filamentary mode, a great number of tiny microdischarges is distributed uniformly over the dielectric surface. A “homogenization” of the filamentary mode will be promoted by low dielectric permittivity and/or small dimensions of gas gap (compare expression 6). It can be affected by the thickness of the dielectric barrier, too. The microdischarge channels have the tendency to emerge always at fixed positions (“spot formation”) because of a memory effect. It is caused by the remaining surface charges. At high amplitude of the applied voltage (and low operation frequency), the microdischarges change their positions randomly on the surface because of the nearly homogeneous distribution of residual charge on dielectric [19]. A pulsed discharge excitation prevents the spot formation at sufficiently short pulse duration/break ratio, too [10]. When the rise time of the voltage becomes comparable to the microdischarge duration, a larger number of microdischarges can be generated simultaneously. Under such conditions a smaller area may be available for the transfer of surface charges, finally resulting in weaker microdischarges [1]. Furthermore, the pulsed discharge operation allows to optimize the energetic efficiency of the production of reactive species.

Up to now it is difficult to generate a stable diffuse barrier discharge at atmospheric pressure. Their existence is limited to a few rare gases (He, Ne) and nitrogen. Excepting ketones, small amounts of impurities can cause the transition to the filamentary BD. For industrial applications this could be a severe drawback as compared to filamentary discharges [53].

3. Application to surface treatment and layer deposition

3.1. Fields of application

The treatment of surfaces by BDs in air has already a long tradition [4–8,35]. This technique is applied, e.g. to improve the wettability, printability and adhesion on polymer surfaces. The BD arrangement is used due to the easy realization of stable and uniform discharge conditions within large areas (compare chapter 2.4). The possibility to treat (and to coat) a surface at low temperature and at pressure close to atmospheric is an important advantage for industrial applications. In particular, no vacuum technique is required. The desired effects result from the activity of the reactive particles (atoms, radicals, excited species, ions) that are generated in the BD by high-energetic electrons. Usually, the surfaces to be treated are non-conductive (plastic materials) or conductive foils (metals) up to 10 m width. They are moved continuously and exposed to the BD at velocities up to 10 m/s. It requires discharge power of about 100 kW at feeding voltage frequencies of 10–40 kHz. Besides foils, also porous materials (textiles, fleeces, felts, membranes, filters, catalysts) are treated [9,10,34,54]. Recently, a special attention has been focused on the application of BDs to the treatment of technical textiles and wool top, as an alternative to the wet chemistry [54,55,56]. In comparison to the common treatment in air, significant improvements can be achieved by using other reactive gases, e.g. acetylene and fluorocarbons. A typical industrial arrangement for these technologies is shown in Fig. 16. Here the non-conducting treated material acts as the dielectric barrier.

The surface treatment is aimed to provide a stable (i.e. long-term) change of the surface tension of treated materials. It improves the adhesion wettability (hydrophilic properties), and consequently the adhesion on the surfaces (Fig. 17). The BD treatment of polypropylene foils in the acetylene atmosphere causes a stable improvement of the surface tension of 72 mN/m. In contrast, the usual treatment in air as well as the treatment in argon appear to be insufficient. A decrease of

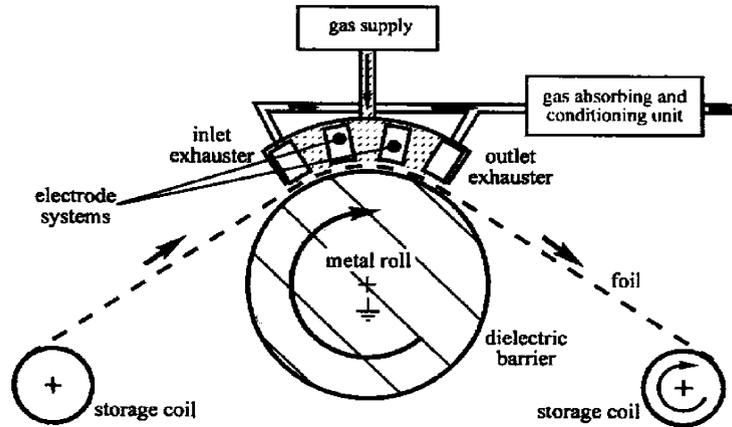


Fig. 16. Arrangement for the foil treatment (Softal) [10].

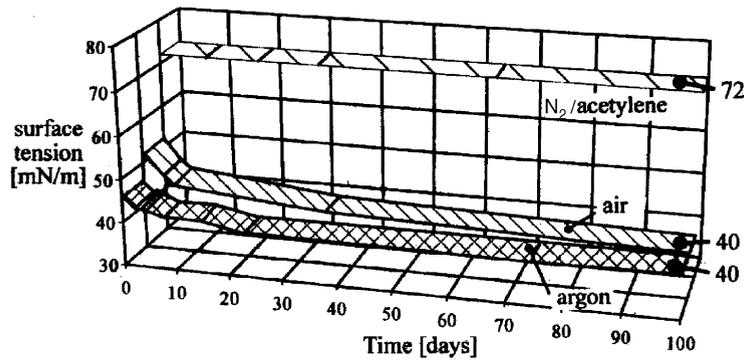


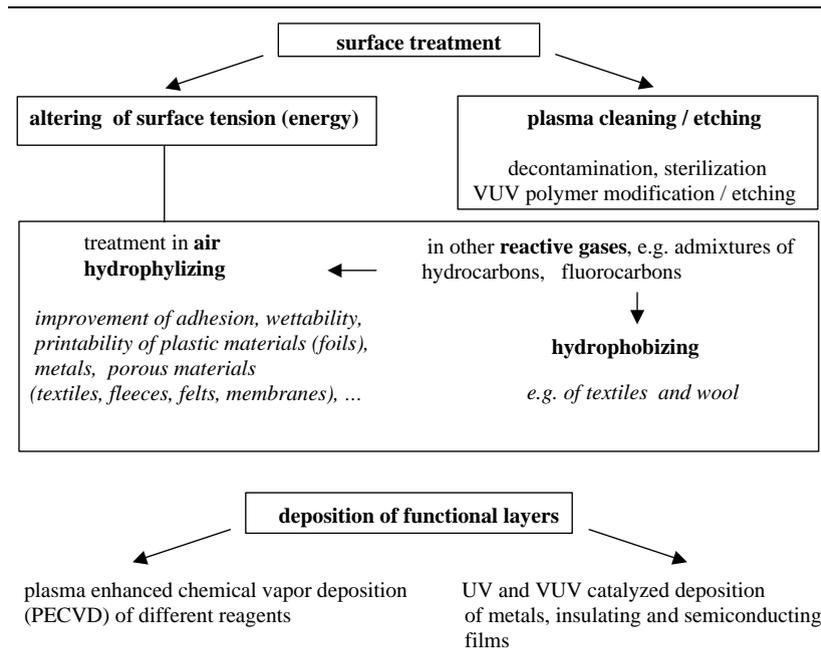
Fig. 17. Surface tension of polypropylene foils in dependence on the storage time after their treatment by air and reactive gases [10].

surface tension results in a decrease of the wettability (hydrophobic effect). This effect can be obtained in fluorine containing gases, and it is used to prevent the contamination of textile materials, in particular.

Other well-known fields of application are the cleaning of metallic surfaces (decontamination) and their sterilization [57–60], as well as the ashing of organic compounds, see e.g. [61]. For example, large-dimensional metal plates can be easily purified from oil and grease contaminations by BD operating in air and oxygen. In this case, atomic oxygen produced in the BD, removes the higher-molecular hydrocarbons by chemical sputtering, transforming them into carbon dioxide and water.

The first attempts of atmospheric pressure plasma deposition started more than 20 years ago [46]. Simple hydrocarbons and fluorocarbons were used to deposit plasma polymers or carbon-like films. Nowadays, an assortment of deposition precursors is known from that a broad variety of films can be formed [9–14,62–67]. With respect to the demands of semiconductor industry, inorganic precursors (e.g. silane) became important for the deposition of insulating materials, e.g. silicon dioxide and silicon nitride [64]. Recently, silane-based coatings on plastic material (e.g. polypropylene) in diffuse BDs have been produced, too [11]. But, some of the deposition precursors based on inorganic constituents are hazardous (e.g. silane). At atmospheric pressure, the relatively

Table 4
Kinds of surface treatment and layer deposition by barrier discharges



high quantities of such precursors can cause serious problems. Therefore, hexamethyldisiloxane (HMDSO) and tetraethoxysilane (TEOS) are studied for their utilizability of a BD-based plasma-enhanced chemical vapor deposition well known from low pressure plasma processing, see e.g. [12, 13]. One important motivation for this is the corrosion protection of metallic surfaces at atmospheric pressure. The layers can be produced of up to μm thickness. Currently, in this field a lot of activities can be observed.

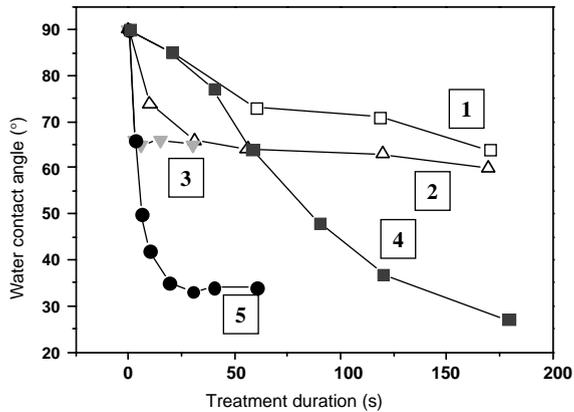
Furthermore, under the conditions of BD operation in noble gases at atmospheric pressure, an intensive UV and VUV radiation due to excimer formation is generated [1,4,53,68,69]. This short-length radiation is used in a wide spreading field of material processing, in particular, for surface modification, polymer etching, or alternatively—for the deposition of thin metallic layers and for the polymerization of laquers (see chapter 3.2.2). The mentioned fields of BD applications for surface treatment and layer deposition are summarized in Table 4.

The surface treatment by BDs will be discussed in more detail for two selected examples, only. The existence of two kinds of BDs—the filamentary and the diffuse (glow) mode is outlined in chapter 2. It is from fundamental interest, in what way do the different forms affect the results of treatment. This question will be clarified for the case of the treatment of polymers. Furthermore, the VUV catalyzed deposition of metallic layers is outlined.

3.2. Selected representative examples

3.2.1. Dependence of surface treatment on operating gas mixture and discharge mode

The uniformity of BD treatment is determined by the discharge properties. In particular, if the discharge operates in the filamentary mode (compare chapter 2.4), then obviously, not every surface treatment is uniform at the microscopic level. The composition of feeding gas mixture affects both the BD mode and plasma properties (density and energy of electrons and ions, type of reactive particles, ...). Therefore, the final quality



| case | BD form | $(O/N)_{surf}$ | $C_{surf}\%$ |
|------|----------------------------|----------------|--------------|
| 1 | He, fil. | 8 | 90 |
| 2 | air, fil. | 9 | 93 |
| 3 | $(N_2+175ppm O_2)$ glow | 1.7 | 87 |
| 4 | He, glow | 0.45 | 87 |
| 5 | N_2 , glow | 0.16 | 71 |

Fig. 18. Water contact angle measurements in dependence on the treatment duration of polypropylene surfaces in diffuse and filamentary barrier discharges in different gas mixtures [71].

of the surface is influenced by a great number of factors. Recently, the first systematic and comparative studies of all these aspects have been published [70,71]. The authors investigated the BD treatment of polypropylene surfaces by the BDs in the filamentary as well as the diffuse mode in different operating gases (air, He, N_2 , N_2 +ppm admixtures of O_2). Polypropylene is of high interest with respect to the potential replacing of halogen containing polymers. The surface transformation was characterized by measurements of the water contact angle and of the chemical surface composition by XPS. Some important results and the corresponding operation conditions are summarized in Fig. 18. For a long enough treatment, two temporally independent values of the water contact angle, 65° and 27° , respectively, are established. These values correspond to the surface energies of 60 and 45 mJ/m^2 , respectively. The latter value indicates a good wettability (hydrophilic properties). The contact angles are depen-

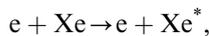
dent on the BD mode and the operating gas mixture. There is a distinct correlation between the measured contact angle and the determined (by XPS) ratio $(O/N)_{surf}$ and $C_{surf}\%$ (see table in Fig. 18). The amount of oxygen on the surface limits the wettability, as it is already well known from the low pressure plasma processing. A good wettability is reached for a relatively high percentage of nitrogen (instead of oxygen) on the surface, corresponding to a smaller percentage of carbon. Generally, these conditions have been realized in the diffuse (glow) mode of BD operation, only. Even, a small admixture of oxygen to nitrogen (case 3, thereby not changing the diffuse discharge mode), drastically increases the $(O/N)_{surf}$ ratio and consequently reduces the wettability. Oxygen containing plasmas induce an effective formation of e.g. hydroxyl-, carbonyl- and carboxylic acid groups on the surfaces (via O atoms, ozone and metastable molecules). In contrast, the BD operation in nitrogen leads to a high nitrogen incorporation on the propylene surface. This process includes N atoms as well as metastable molecules. It results in the formation of functional amine-, amide- and nitrile groups on the substrate surface. The diffuse BD in helium (cases 2 and 4) also leads to the dominant incorporation of nitrogen that is based on the formation of functional groups from the residual gas admixtures. Because of the effective production of reactive species near the electrodes (i.e. the substrates), the glow regime as compared to the filamentary mode, seems to be advantageous (compare Fig. 15). It results in effective surface reactions at comparable low power densities. The formation rate of the final surface conditions (e.g. expressed in the equilibrium contact angle) mostly depends on the specific power density (per area unit). In contrast, the equilibrium situation itself seems to be independent of the power density for the conditions under consideration (compare curves 5 with 4). The presented results illustrate the great complexity of the factors affecting the final surface transformation by the BD plasma treatment.

3.2.2. Photo-induced layer deposition

When BDs are operated in noble gases or noble gas/halogen mixtures at atmospheric pressure, an

intensive incoherent excimer radiation at different UV and VUV wavelengths is generated. Every microdischarge acts as an intense radiation source. Typical examples are the Xe_2^* , KrCl^* or XeCl^* complexes, radiating at 172, 222 or 308 nm, respectively. First applications of BDs to the generation of VUV excimer radiation were reported already in 1955 [72]. These radiation sources, called excimer lamps, have found a wide spreading field of applications since the end of the 1980s. With respect to surface treatment and deposition processes, it is essential that the excimer radiation can initiate photophysical and photochemical processes by breaking molecular bonds thus modifying surface properties. The following examples of application are listed here: the photopolymerization of special paints, printing inks, varnishes and adhesives [1,73–76]; surface cleaning/modification [77,78]; thin insulating or semi-conducting film deposition [79–82]; photo-induced area-selective metal deposition [83–87].

The formation of excimers in BDs is favored by high collision rates at elevated pressure in connection with the efficient ionization of the precursors under the non-equilibrium discharge conditions. Exemplary, the excimer formation mechanism is presented below for the feeding gas Xe:



(8)

The excimer radiation is transmitted from the BD volume to the outside by transparent to UV materials (quartz windows, transparent or net-shaped electrodes). Cylindrical BD configurations with annular discharge gaps as well as flat panels are used. In Fig. 19a typical cylindrical arrangement is shown. Several discharge tubes may be located so as to arrange large-dimensional plane UV/VUV treatment sources (Fig. 19b).

The photo-induced deposition of metallic layers belongs to the most spectacular applications of VUV radiation, generated in BDs [83–87]. The VUV radiation of an Xe source is used for the area-selective dissociation of a palladium acetate film. In this way a thin palladium film is

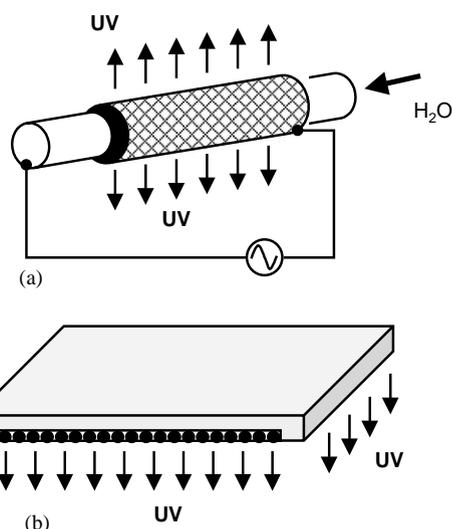


Fig. 19. Schematic arrangement of a BD excimer radiation source (a—cylindrical configuration with annular discharge gap; b—plane irradiation unit with eight radiation sources) [86].

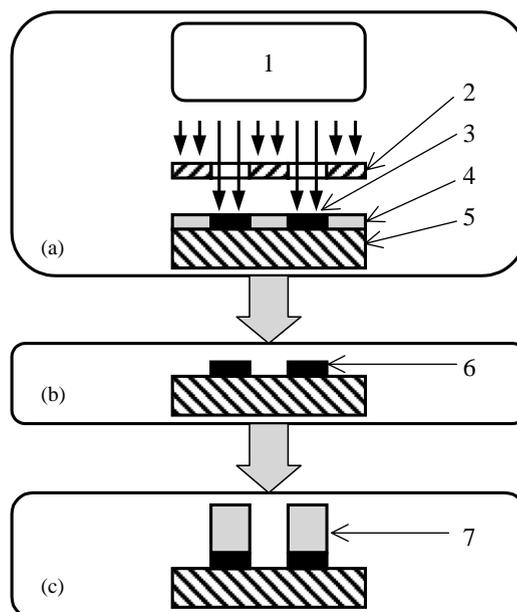


Fig. 20. Scheme of the photo-induced area-selective surface metallization by barrier discharge excimer radiation (**step a**: VUV irradiation, 1—BD source of excimer radiation, 2—structured mask, 3—irradiated palladium acetate=metallic palladium, 4—soluble non-irradiated palladium acetate, 5—substrate; **step b**: removal of the soluble layer, 6—metallic palladium activator; **step c**: galvanic process, 7—new created metallic structure) [86].

produced. This film acts as an activator for the metallic layer deposition in a subsequent galvanic procedure. Thus, in only a few process steps metallic layers e.g. of copper, nickel or gold of μm thickness and complex structure can be formed. Because of low gas temperatures, these layers can be produced on sensitive materials, as cardboard and fleeces, too. The principal steps of the photo-induced metallization process are illustrated in Fig. 20.

4. Summary and conclusions

BDs produce highly non-equilibrium plasma conditions in a controllable way at atmospheric pressure, and at moderate gas temperature. There are two modes of BDs. The common mode is the filamentary one, but under very special conditions a diffuse mode can be generated. The physical properties of both modes, as well as the main discharge mechanisms, have been discussed. In particular, recent results on spatially and temporally resolved emission spectroscopic investigations were presented. The main electric parameters, necessary for the controlled BD operation, were listed.

The BDs provide energetic electrons, which are able to generate atoms, radicals and excited species. If noble gases (or noble gas/halogen gas mixtures) are used as working gas, they are sources of an intensive short-length excimer radiation. Both, the reactive species and the excimer radiation, have been applied for a long time in many fields of plasma treatment and layer deposition, which was presented in an overview on these fields. Selected examples were outlined in more detail. With respect to a uniform surface treatment, diffuse discharge (or homogenized) conditions are very desirable. This was shown on the base of recent literature data for the treatment of polypropylene surfaces. Furthermore, the VUV catalyzed deposition of metallic layers, which belongs to the most spectacular application of VUV radiation, was discussed.

BDs have a great flexibility with respect to their geometrical shape, working gas mixture and operation parameters. The scaling-up to large

(industrial) dimensions is no problem. The possibility to treat or coat surfaces at low gas temperature and pressures close to 1 atm is an important advantage of their application. The applications described in this paper base on intensive activities for a better understanding of the discharge physics and plasma chemistry. There is a great potential for BD plasma processing in future.

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