Applications of Microplasmas and Microreactor Technology

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During the last decade a number of microcavity plasma devices have been developed. Examples are micro-
hollow cathode (MHC) discharges and cathode boundary layer (CBL) discharges proposed by Schoenbach,
capillary plasma electrode (CPE) discharges proposed by Kunhardt and Becker, and micro-structured electrode
arrays (MSEs) introduced by Gercke and Penache. Arrays of microplasmas based on silicon, ceramic, or
metal/polymer structures were investigated by Eden, Frame, Park and coworkers. A breakthrough in the life
expectancy of such devices was achieved when all metal electrodes were covered by dielectrics, thus combining
dielectric-barrier discharge technology with microcavity plasma devices.

The advantage of this technology is that large numbers of miniature atmospheric-pressure non-equilibrium
discharges can be operated in parallel. Applications include emitters for visible and UV radiation, photode-
tectors, sensors, decontamination, surface modification, etching, film deposition, generation of nanoparticles.
Operated in different gas mixtures many of these devices proved to be efficient emitters of ultraviolet excimer
radiation. If a small gas flow is fed through these microplasmas applications for plasmachemical synthesis and
pollution control become feasible. Novel applications are expected from the combination of microreactor tech-
nology with non-equilibrium plasma chemistry. Doping or coating of the dielectric surfaces results in additional
catalytic effects.

1 Introduction

Miniaturized plasma sources or microplasmas have found a number of important applications [1, 2]. Some of
them are scaled-down versions of well known larger configurations, others inherently depend on confined small
dimensions. A typical example of the first kind is microplasma welding which now is used for materials of 0.02
to 1 mm thickness. It uses a miniaturized version of the conventional MIG or TIG (metal inert gas, tungsten
inert gas) welding configuration and can be used for precision welding of thin sheets or foils of non-alloyed and
alloyed steels, as well as gold, platinum, titanium, niobium and many other materials. Other representatives of
this category are microplasma torches developed to cut thin sheets of 0.1 mm thickness. Miniature RF torches
are also widely used as inductively coupled plasmas (ICPs) for on-line spectrochemical elemental analysis of
gaseous, liquid or solid samples. An application that has always used small dimension plasmas is the process of
spark erosion, spark-assisted etching or electrical discharge machining (EDM). In recent years better numerical
process control and miniaturization of the electrodes have resulted in meso-machining capabilities, also referred
to as micro-EDM. Wire electrodes as thin as 25 µm are used with advanced spark control limiting the ‘overburn’,
the gap between tool electrode and work piece, to as little as 3 µm. The micro-EDM process has been used for
fabrication of meso-scale parts of dimensions 10 µm to 100 µm from difficult-to-machine materials includ-
ing hardened tool steel, titanium, tungsten, diamond, doped silicon, gallium arsenide and rare earth magnetic
materials [3, 4].

The microdischarges observed in most atmospheric-pressure dielectric-barrier discharges (DBDs) are also typ-
ical representatives of microplasmas [5, 6]. Their properties have been studied for a long time. Recent advances
in diagnostics, modeling and manufacturing technology have been driven by industrial ozone generation [7] and, even more so, by large-scale applications in flat plasma display panels (PDPs) [8]. This overview concentrates on miniature non-equilibrium plasmas generated in spatially confined geometries at about atmospheric pressure: their generation, their properties and their applications. The recent interest in atmospheric pressure glow discharges stems from the intriguing prospect of performing plasma processes normally performed at low pressure at a much faster rate and without the need for expensive vacuum systems.

2 Miniature atmospheric dc glow discharges between metal electrodes

Atmospheric-pressure discharges in air between metal electrodes tend to turn into arc discharges which require a lower burning voltage because of a more efficient process for electron release at the cathode (thermoionic emission) and in the volume (thermoionization). Grotrian [9] was probably the first to point out as early as 1915 that in nitrogen also stable glow discharges can be obtained at atmospheric pressure when the current is limited to low values by a large resistor. An extensive investigation on the transition from a glow discharge to an arc discharge was performed by Hsu Yun Fan at MIT in 1939 [10]. With water cooled copper electrodes Fan was able to get stable miniature glow discharges in hydrogen up to a pressure of 13 bar and in air, oxygen and nitrogen at 1 bar. In a recent paper Staack and coworkers [11] investigated stable glow discharges with small inter-electrode gap spacing down to 20 \( \mu \text{m} \). If the spatial dimension of the discharge is kept small enough transition to an arc discharge can be avoided. Fig. 1 shows pictures of such discharges in atmospheric-pressure air.

Fig. 1  Glow discharges in atmospheric pressure air (reprinted by permission from D. Staack, B. Farouk, A. Gutsol, A. Fridman, "Characterization of a DC Atmospheric Pressure Normal Glow Microdischarge", Plasma Sources Sci. Technol. 14, 700–711 (2005); Institute of Physics Publishing, Ref. 11.

The thickness of the cathode fall region, not resolved in the pictures, is of the order 10 \( \mu \text{m} \). The bright region is a normal glow discharge, thermally stabilized by its size with a typical diameter of the order 100 \( \mu \text{m} \). The measured rotational temperature was about 1550 K. Current density and reduced electric field roughly correspond to values derived from similarity laws for glow discharges starting from low pressure air data \( j/p^2 = 300 \ \mu \text{A cm}^{-2} \text{Torr}^{-2} \) and \( E/p = 10 - 30 \ \text{V cm}^{-1} \text{Torr}^{-1} \), provided that a correction is made for the high gas temperature.

3 Microdischarges in dielectric-barrier discharges (DBDs)

The dielectric barrier used in many types of barrier discharges is a safe and reliable way to prevent arc formation. Different configurations are used, all of which have as a common feature at least one dielectric plate or coating and a discharge space in the current path between the electrodes. In such configurations breakdown at atmospheric pressure normally occurs in many short-lived current filaments referred to as microdischarges. Only in some gases (He, Ne, Ar, pure N\(_2\)) under special operating conditions also diffuse (homogeneous) glow discharges can be obtained at atmospheric pressure [12, 13].

Fig. 2 shows different planar electrode configurations with one or two dielectric barriers made from fused silica, Pyrex glass, ceramic, enamel or even polymer coatings. Since the dielectric does not pass a dc current ac
applied voltages are required. The driving frequency can range from line frequency to several GHz. The electrode spacing typically ranges from a fraction of 1 mm to several cm. The lower part of Fig. 2 shows the so-called coplanar configuration with parallel electrode strips embedded in a dielectric or printed on top and covered with a dielectric layer. Very fine meander-like electrode structures can be manufactured with more than 1 m of electrode length on 1 cm$^2$ surface area. For these discharges the term micro-structured electrode (MSE) discharges was introduced [14–16].

In the common filamentary mode of a DBD many bright microdischarges are observed. During the past decades important information was collected on the nature of these short-lived current filaments [5, 17]. Early image converter recordings of microdischarges in air and oxygen were obtained by Tanaka et al. [18]. Current measurements were performed on individual microdischarges [19–21]. The transported charge and its dependence on dielectric properties was determined over a wide parameter range [22, 23]. Typically, many microdischarges are detected per square cm of electrode area. Their number density depends on the power dissipated in the discharge. The order of magnitude is $10^6$ microdischarges per cm$^2$ per second [24]. The influence of humidity and that of UV radiation was investigated [25]. In recent years refined spectroscopic diagnostics yielded information on species concentrations and plasma parameters inside individual microdischarges [26–29]. For a given configuration and fixed operating parameters all microdischarges have similar properties. They start at a well defined breakdown voltage, and they stop within a few ns after a well defined current flow or charge transfer. Each current filament of approximately 100 µm radius can be considered a self-arresting discharge, terminated at an early stage of discharge development by charge accumulation on the dielectric surface(s), which results in a local collapse of the electric field. A microdischarge has properties resembling those of a glow discharge with a thin cathode fall region of high electric field and a positive column of quasi-neutral plasma. Depending on the cooling the gas temperature can remain low, even close to room temperature. The electron energy in the microdischarges is a few eV. Important microdischarge properties of a DBD in a 1-mm air gap are summarized in Table 1.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Microdischarge properties in a 1-mm discharge gap in atmospheric-pressure air.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Duration:</td>
<td>1-100 ns</td>
</tr>
<tr>
<td>Filament Radius:</td>
<td>about 0.1 mm</td>
</tr>
<tr>
<td>Peak Current:</td>
<td>0.1 A</td>
</tr>
<tr>
<td>Current Density:</td>
<td>100-1000 A cm$^{-2}$</td>
</tr>
<tr>
<td>Total Charge:</td>
<td>0.1-1 nC</td>
</tr>
<tr>
<td>Electron Density:</td>
<td>$10^{14} - 10^{15}$ cm$^{-3}$</td>
</tr>
<tr>
<td>Electron Energy:</td>
<td>1-10 eV</td>
</tr>
<tr>
<td>Gas Temperature:</td>
<td>close to average gap temperature</td>
</tr>
</tbody>
</table>

In plasma display panels, due to the smaller dimensions (gap spacing about 0.1 mm) and different gas filling (Xe/Ne mixture at 560 Torr) the values for the current density, electron density and transferred charge are roughly ten times smaller [30, 31]. The radius of the current filament and the electron energy, however, are comparable.
4 Miniature discharges in small confined geometries

Novel types of atmospheric non-equilibrium discharges have been developed in the form of microhollow cathode (MHC) discharges first proposed by Schoenbach and coworkers [32] in 1996 and in the form of capillary plasma electrode discharges, patented by Kunhardt and Becker [33] in 1999.


The MHC concept extends hollow cathode discharge operation, normally restricted to low pressure, to atmospheric pressure by using tiny cylindrical holes of typically 0.1–0.25 mm diameter (D) in a flat sandwich configuration containing for example a thin alumina dielectric between two molybdenum foils (Fig. 3, upper left). Following the early work at Old Dominion University, Norfolk, several groups in various countries have taken up the subject [34]. Parallel as well as series operation of such discharges has been demonstrated. The non-equilibrium nature of the plasma has been assessed by measuring the gas temperature (about 2000 K), the electron density (dc about \(10^{15}\) cm\(^{-3}\), during short pulses up to \(5 \times 10^{16}\) cm\(^{-3}\)) and the mean electron energy (0.5 – 5 eV).

Recent numerical simulations by Kushner [35] show that also this discharge has many similarities with a glow discharge: a thin localized cathode fall region of high field strength and a moderate gas temperature. When both electrodes are perforated a dc MHC discharge pumps gas through the aperture.

When the hole diameter D of an MHCD is widened to about 1.5 mm (Fig. 3, lower left) a new type of discharge is observed which, depending on the gas, current and pressure, can exhibit a varying number of beautifully arranged self-organized bright discharge elements [36]. Since these bright spots originate in the cathode fall region Schoenbach called this configuration the cathode boundary layer (CBL) discharge [37].

A completely different type of discharge, also using small holes in a dielectric plate, was proposed by Kunhardt [38] and Becker (Fig. 3, right part). It is closer to the classical DBD configuration. One dielectric plate has many parallel thin capillary channels. It could be shown that, when the frequency is raised above a few kHz, all of a sudden, capillary plasma jets emerge from the capillary holes. They overlap and merge to form a volume plasma with electron densities by orders of magnitude higher than those observed in the diffuse DBD mode. The discharge can be operated also with both dielectrics perforated or even as a dc discharge, when the upper dielectric in fig. 3 is removed and the perforated dielectric plate is on the cathode side. Each of the holes acts as a current limiting micro-channel that prevents the overall current density from increasing above the threshold for the glow-to-arc transition.

4.1 Microcavity plasma devices based on silicon technology

A group at the University of Illinois at Urbana-Champaign investigated the use of p-type Si(100) wafers for a variety of microcavity devices. Silicon was the material of choice because micromachining technologies are available for producing a large number of small structures [39], [40]. Fig. 4 shows a flat MHC structure (left), an inverted pyramidal structure (centre) and a deep blind hole (right). The structures were produced by lithographical patterning. For the inverted pyramids anisotropic wet etching with KOH was used, for the others deep reactive ion etching with \(\text{O}_2\). The area of the inverted pyramids is \(50 \times 50 \, \mu\text{m}^2\) or \(100 \times 100 \, \mu\text{m}^2\), more recently down to
10x10 µm². Typical cavity dimensions were 13-400 µm wide and between 0.2 and 2 mm deep. It turned out that parallel operation was more stable and that higher currents could be drawn when the polarity was reversed and the Si wafer was used as the anode [41]. A common feature of all these dc discharges operating at local power densities exceeding 10 kW cm⁻³ is, that electrode erosion becomes a problem after some time. A major breakthrough was achieved with the pyramidal cavity configuration, when the whole structure was covered with an additional Si₃N₄ layer of 2-4 µm thickness and the device was operated like a DBD with a 5 - 15 kHz sine voltage of about 200 Vrms. Arrays of several thousand discharges could be operated simultaneously for an extended period of time [42], [43]. Specific local power loadings of 250 kW cm⁻³ have been reached. There is no doubt that ac operation and the use of refractory materials will be the future.

4.2 Microcavity plasma devices based on aluminum electrodes with alumina coating

Another interesting approach is the use of Al foils or Al structures that can be covered with a thin alumina coating serving as a dielectric layer. Park and Eden [44] used perforated 70 µm thick Al foils that were anodized in an oxalic acid solution. The process could be controlled to consistently yield Al₂O₃ films of 10 µm thickness also covering the cylindrical holes. No part of the electrodes is exposed to the plasma. The left part of Fig. 5 shows a sandwich of two such electrodes, the upper one with round holes of 100 µm diameter, the lower one with slightly larger holes of 200 µm diameter. The whole electrode configuration is extremely thin and flexible. The device can be operated with a 5 - 50 kHz sine voltage of 275 V amplitude. A large number of discharges could be operated simultaneously in Ne or air with an intensity variation from hole to hole of only 10% [45].

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A slightly more rigid Al structure, shown in the right part of Fig. 5, is used by Tachibana and coworkers [46]. It has the form of a metal mesh of 250 µm thickness containing small rectangular openings 500x2000 µm². The structure was coated with a 150 µm thick Al₂O₃ dielectric layer by plasma spraying. After spraying the openings had a size of 200x1700 µm². Two coated Al electrodes are mounted back to back with openings aligned so that miniature DBDs can be initiated between the plates along the inner surface of the openings. Tachibana uses bipolar rectangular voltage pulses of 4 µs duration and 20 kHz repetition frequency. At atmospheric pressure the minimum firing voltage was 500 V in He or 1200 V in N₂. Again, it is no problem to have simultaneous discharges in a large number of openings in an electrode set of 5 cm diameter. The arrows in Fig. 5 indicate that a gas flow can be forced through the apertures, which turns the devices into a multitude of plasmachemical microreactors.

4.3 Microtorch configurations

Atmospheric-pressure plasma jets operated mainly in rare gases can produce flows of non-equilibrium plasma [47]. Miniaturization has led to number of interesting microtorch designs. Sankaran and Giapis [48, 49] at California Institute of Technology used stainless steel capillary tubes ranging from 178 µm to 508 µm inner diameter as cathodes and a metal mesh or a temperature controlled Mo substrate as anode (Fig. 6, left). The electrode distance could be varied from a fraction of 1 mm to several mm. With an Ar flow into atmospheric pressure air stable operation of this flow-stabilized plasma microjet was achieved over hundreds of hours. Currents up to 20 mA were reached for individual jets, parallel operation was demonstrated with ballast resistors.

The configuration shown in the middle part of Fig. 6 is investigated by Yokoyama and coworkers [50] at Tokyo Institute of Technology. It uses a stainless steel nozzle of 200 µm inner diameter and 350 µm outer diameter as one electrode and a wire mesh, or alternatively a needle, as the counter electrode. Working in atmospheric air, Ar or He was fed through the nozzle and the electrode distance was varied between 0.1 to 1 mm. Supplied with a regulated dc voltage at certain operating conditions regular current pulses were observed, at other conditions continuous operation.


In addition to the described dc microtorches a number of rf or microwave driven miniature atmospheric pressure plasma jets have been described in the literature, like the "plasma needle" proposed by Stoffels and coworkers [51] at Eindhoven University of Technology and various "plasma pens" investigated by different institutions. Also thin flat linear jets in narrow slot arrangements (100-600 µm in width) and up to 35 cm length have been reported [52]. A multiple torch based on DBD technology (Fig. 6, right) has recently been described by Chichina and coworkers [53] from Prague. Helium with some additives flows through a number of silica glass tubes of 1.5 mm internal diameter. RF power of 13.56 MHz frequency is applied to an external sleeve electrode surrounding the tubes while the substrate is grounded. The electron density in the jet was about 2·10¹³ cm⁻³ and the distance to the substrate 5 mm.
5 Discharge physics of microplasmas

With shrinking geometrical dimensions and rising pressure conditions are reached where the linear device extension approaches the mean free path of electrons and becomes commensurate with the Debye length of the plasma. Some of the familiar concepts like breakdown criteria and scaling laws for glow states may no longer apply. The electron densities may not be sufficient to ensure full shielding of these tiny plasma volumes. Breakdown voltages in narrow gaps have been investigated, experimentally [54] as well as theoretically [55]. In very narrow gaps the onset of ion-enhanced field emission and quantum tunneling of electrons from the electrodes to the gas phase change the left branch of the Paschen curve by considerably lowering the expected breakdown voltage. The effects are more pronounced in He and Ne than in Ar and N$_2$ [56]. Limits for scaling laws of glow discharges are reached when the thickness of the cathode fall region become comparable to linear device dimensions [57]. In this case small changes in operating parameters can cause significant variations of plasma parameters. Control of instabilities, pattern formation and self-organization as well as short pulse behavior belong to the questions that require further attention. An open question is: How small can a cavity become in which we still can ignite a discharge?

6 Applications of microplasmas

The various devices used to generate microscale plasmas described in the previous sections led to a number of important, sometimes novel applications. Most of these devices can be used as bright and efficient sources of excimer radiation [58], [59], [60], [61] or Lyman $\alpha$ ($\lambda = 121$ nm) radiation [62], some of them also as radiation detectors [63]. Large arrays can find applications as microdischarge lamps or microdisplays. Si-based microcavity plasma devices have reached a packing density of $10^4$ cm$^{-2}$. Further progress is expected [42]. The direct coupling of microdischarges to semiconductor devices has been demonstrated [64]. The size of individual microdischarges is approaching cellular dimensions, which suggests novel applications in medicine and biology. Other applications may include sensors for explosives and for chemical and biological agents. Microplasmas operating at atmospheric pressure offer advantages as miniature sources of ions, excited species and radicals. This led to applications for selective surface cleaning, modification, etching, printing and deposition [48], [49], [53], [65], [66], [67], [68]. The use for spectroscopic analysis and biomedical diagnostics has been suggested [69], [70], [71], [72]. The small size allows on-chip chemical analysis and incorporation in miniaturized total analytical systems ($\mu$-TAS) [73], [74], [75]. In the manufacturing of microfluidic devices microplasmas initiated inside small channels are used to functionalize internal surfaces [76]. A number of investigations have concentrated on the use of microplasmas as microreactors for gas phase chemistry. Examples of their use in plasmachemical synthesis are the generation of ozone [77] or the hydroxylation of benzene and toluene [78]. The short transit time in the plasma zone was also used for the generation of ultra small Si nanoparticles with controlled diameters of only a few nm [77]. By using many parallel microdischarges important applications are foreseen in pollution control, e.g. the abatement of CF$_4$, NO$_x$ and hydrocarbons [16], [79]. Since plasmas can inactivate microorganisms like cells, bacteria, spores, viruses, microplasma or MSE arrays have also been investigated with respect to the decontamination and sterilization of surfaces [56], [80].

7 Summary and outlook

Recently a variety of microcavity plasma devices have been investigated. Some of them combine recent developments in plasma science and in materials processing with microfabrication technologies. Using Si technology it has been demonstrated that miniature atmospheric pressure non-equilibrium plasmas (glow discharges) can be sustained and that large arrays of parallel discharges can be operated simultaneously. In flow systems these discharges can be used as a multitude of plasmachemical microreactors. Despite of its excellent mechanical properties and established micromachining capabilities silicon, being a semiconductor, may not be the ideal material for some applications. Operation of atmospheric pressure discharges in 3-D structures like reticulated ceramic foams and ceramic monoliths has also been reported, with and without catalytic coatings [81], [82]. Atmospheric pressure glow discharges can enter pores as small as 15 $\mu$m [83]. The combination of these advances with recent progress in the fabrication of microchannels in microfluidic devices [84] is expected for the near future. Micromachining procedures have also been developed for other materials including glass, fused silica [85], polymers [86].
Multilayer glass devices with 3-D microchannel networks have recently been reported by Kikutani et al. [87]. Using similar technologies, combined with DBD excitation, glow discharges in catalyst-coated microchannels can be interlaced with cooling channels and thus open a unique possibility to combine microreactor technology with non-equilibrium plasma chemistry and catalysis.

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