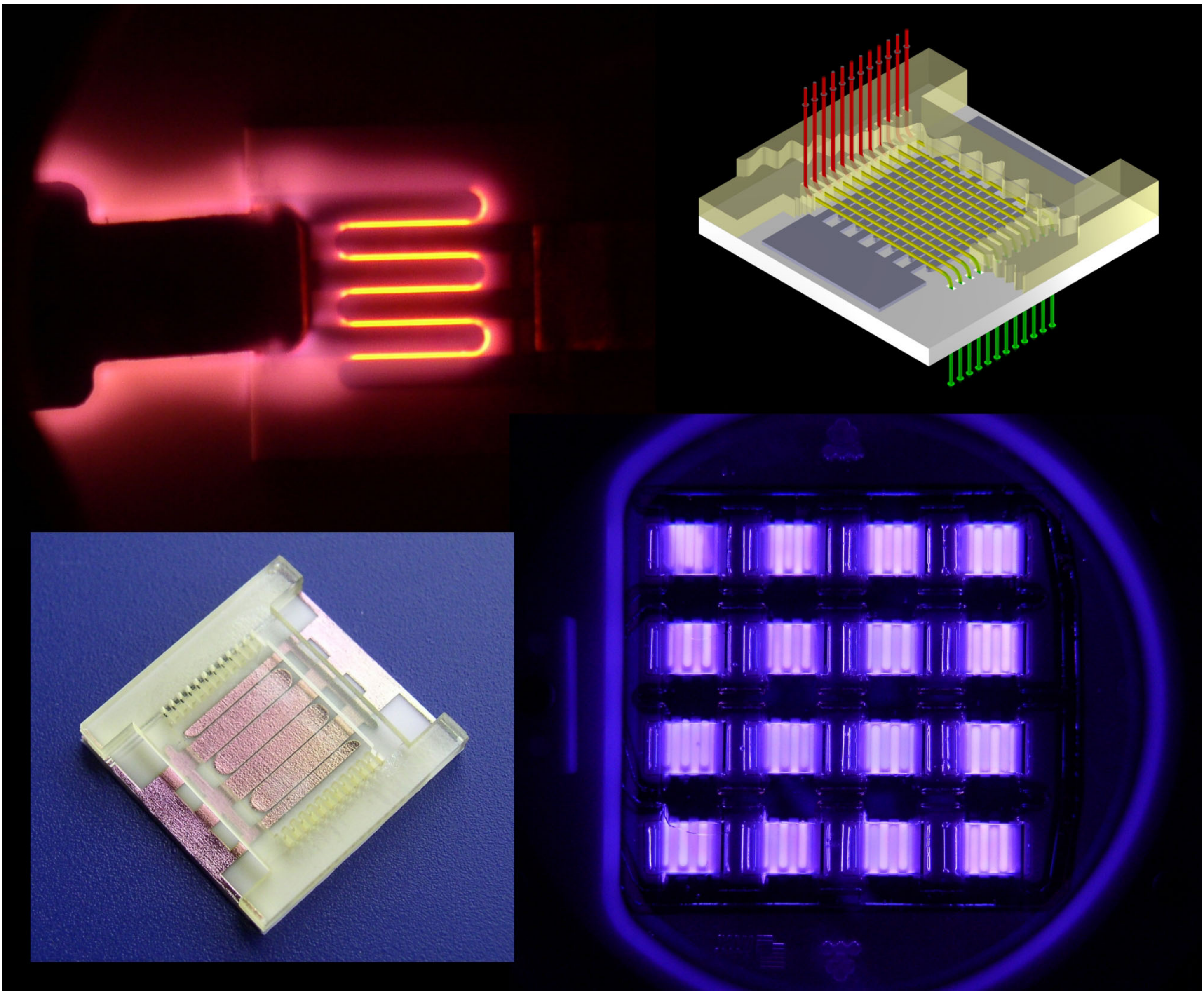
Lutz Baars-Hibbe

Characterization and Applications of High Frequency Discharges in the Near-Atmospheric Pressure Range Using Micro-Structured Electrode Arrays



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Characterization and Applications of High Frequency Discharges in the Near-Atmospheric Pressure Range Using Micro-Structured Electrode Arrays

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von Lutz Baars-Hibbe
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Contents

Acronyms

AC	alternating current
amu	atomic mass units
CFD	computational fluid dynamics
DBD	dielectric barrier discharges
DC	direct current
DLC	diamond-like carbon
EI	electron impact ionization
HF	high frequency
HFC	hydrofluorocarbon
ICP	inductively coupled plasma
IMT	Institut für Mikrotechnik, TU Braunschweig
LIF	laser induced fluorescence spectroscopy
MFC	mass flow controller
MID	multiple ion detection
MSE	micro-structured electrode
OES	optical emission spectroscopy
PECVD	plasma-enhanced chemical vapor deposition
PFC	perfluorocompound / perfluorocarbon
PTFE	polytetrafluoroethylene (“teflon”)
QMS	quadrupole mass spectroscopy
RF	radio frequency (13.56 MHz)
RIE	reactive ion etching
rms	root mean square: labeling used for effective electric values
sccm	standard cubic centimeter per minute
SEM	scanning electron microscopy
TEOS	tetraethoxysilane
UV	ultraviolet

1. Introduction

1.1 Preface

Plasma (discharge) processes play key roles in the production of many commodities (e. g. computer chips, automobiles, textiles, packaging materials). In Germany, currently 70 to 80 thousand workplaces can be directly associated with plasma technology [1]. Worldwide sale of plasma sources and systems is estimated to be 27 billion € in 2005 [2]. However, only few commodities are directly associated with the term “plasma” or apply plasma in order to perform useful tasks such as plasma display panels or light sources like high-pressure gas discharge car headlights or video projector lamps. Since plasma process tools are integrated into many production procedures / lines of intermediate goods as well as final products, a more realistic number is currently closer to 500 thousand employees, or nearly 7 % of jobs in the German manufacturing sector. This represents more than 50 billion € per year for the German economy, with an estimated annual growth rate of 10 % [1].

Plasma systems are traditionally divided two major categories: thermal and non-thermal systems. Thermal plasmas (e. g. arc discharges, plasma torches) are associated with thermal ionization and enable the input of high power at high operating pressures. However, low selectivity, very high gas temperatures, serious quenching requirements, and electrode problems result in limited energy efficiency and applicability of thermal plasma sources [3]. Non-thermal plasmas consist of highly energetic electrons with energies of several eV (several 10 000 K), while the temperatures of the ions are far below the electron temperatures, and the neutral gas particles may exhibit even room temperature (300 K). Non-thermal plasmas offer high selectivity and energy efficiency in plasma-chemical reactions; they can be operated effectively at low temperatures and without any special quenching [3]. This plasma type is capable of performing tasks which are inaccessible by other means (e. g. achieving high aspect ratios for the production of large scale integrated circuits in semiconductor industry).

Non-thermal plasmas can be divided into two categories: homogeneous gas-phase reactions and heterogeneous reactions involving the interaction of plasma with a solid surface [1]. The plasma-solid interactions can be divided into three subcategories: plasma-induced etching or ablation (see Chapter 5.1), plasma-enhanced chemical vapor deposition (PECVD, also called thin film deposition), and surface modification (e. g. increase or decrease of the surface tension / energy / wettability by plasma-chemical and / or plasma-physical treatment of the material).

However, non-thermal plasmas are economically divided into two other categories: low pressure plasmas and atmospheric pressure plasmas. Most industrial applications of non-thermal plasmas are low pressure applications using their advantages [4]: low breakdown (ignition) voltages (see Chapter 2), stable plasma operation, electron temperatures capable of dissociating molecules (1 eV – 5 eV) at room temperature, relatively high concentrations of ions or radicals to drive etching and deposition reactions (see Chapter 5.1), and particularly, a uniform glow discharge over a large gas volume or electrode area in order to guarantee highly reproducible and stable manufacturing processes and required uniform product qualities. Important examples can be found in microelectronics and automotive industry [1, 5]: dry etching processes and PECVD in fabrication of semiconductor devices, and diamond-like carbon (DLC) coating of unit injectors for diesel engines. Another example is thin film deposition of SiO_2 coatings on food packaging materials as gas and vapor barriers in order to reduce the permeation rate of gases or vapors such as O_2 or H_2O and aromas [1]. Biomedical applications such as the fabrication of non-fouling coatings or plasma sterilization are increasingly used as a replacement of destructive or harmful procedures involving radiation or toxic chemicals.

Operating the plasma at low pressure has several disadvantages [4]. Vacuum systems are expensive and require maintenance. Load locks and robotic assemblies must be used to shuttle materials in and out of vacuum. Additionally, the size of the object that can be treated is limited by the size of the vacuum chamber.

At atmospheric pressure, cost-intensive vacuum technology can be avoided, and thin film deposition with very high rates is possible. Non-thermal atmospheric pressure plasmas have been studied for a variety of industrial applications such as pollution control, volatile organic compounds removal, car exhaust emission control, and polymer surface treatment (to promote wettability, printability and adhesion) [3]. Atmospheric pressure plasma is the most important topic for future economic exploitation of plasma technology and of future plasma research, as viewed by German and international experts [6].

Many approaches have been proposed in the last 15 years to overcome the problems of generating and sustaining a stable uniform and homogeneous non-thermal atmospheric pressure plasma. Massines *et al.* [7, 8], Okazaki *et al.* [9, 10], Trunec *et al.* [11] and Roth *et al.* [12] successfully generated atmospheric pressure glow discharges with a dielectric barrier array, and Selwyn *et al.* [4, 13, 14] developed a radio frequency atmospheric pressure plasma jet producing a stable and homogeneous plasma. There are two approaches based on the Paschen similarity law (*pressure · electrode distance* = *const*., see Chapter 2.3) which scale down the electrode dimensions in the µm-range in order to ignite discharges at atmospheric pressure, at moderate voltages, working in the Paschen minima of the different gases. Schoenbach *et al.* [15, 16], Schmidt-Böcking *et al.* [17] and Eden *et al.* [18, 19] use a micro-hollow-cathode array in order to generate atmospheric pressure glow discharges.

Recently, our research group introduced micro-structured electrode (MSE) arrays as alternative atmospheric pressure plasma sources, consisting of a system of planar and parallel electrodes (comb-like structure, see Figure 1.1) [20 – 25]. The electrodes are arranged on an insulating substrate and manufactured by means of modern micro-machining and galvanic techniques. The electrode dimensions, particularly the electrode gap width *d* in the µm-range, are small enough to generate sufficiently high electric field strengths to ignite atmospheric pressure glow discharges applying only moderate voltages (less than 400 V) at high frequency (13.56 MHz).

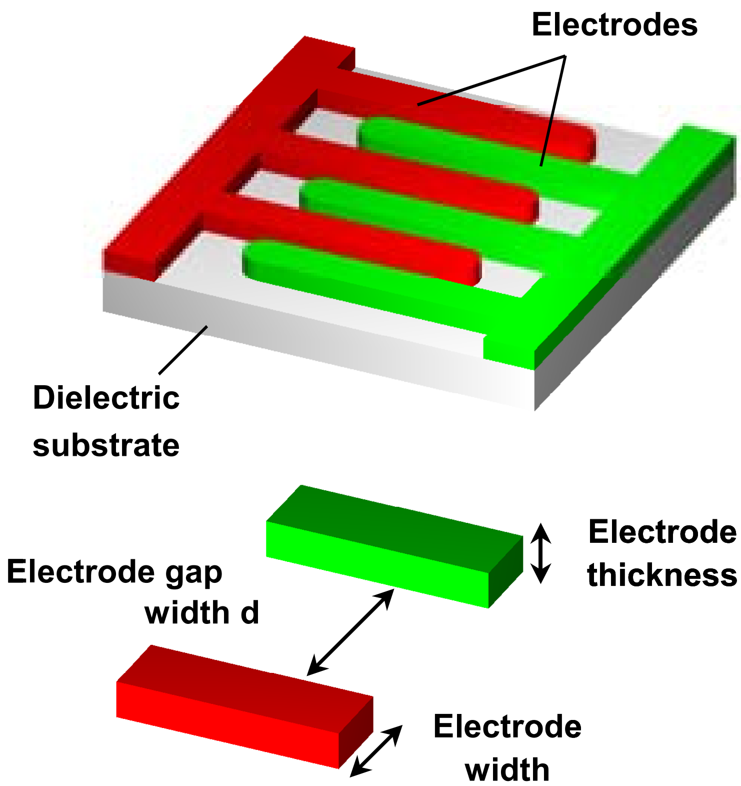

Figure 1.1. *Top: schematic view of a micro-structured electrode (MSE) array. The electrodes (comb-like capacitor structure) are arranged on an insulating substrate. Bottom: the characteristic electrode dimensions are electrode thickness and electrode width, and particularly, the electrode distance: electrode gap width d.*

MSE arrays are suitable non-thermal plasma sources for various applications. Thin film deposition of DLC coatings on various substrates and surface modification of plastic films modifying the wettability were successfully carried out [22 – 24].

The applicability of the MSE plasma source for the treatment of waste (exhaust) gases was already demonstrated by the successful decomposition of NO [21 – 23]. Since 1997 a total of 141 countries have ratified the Kyoto Protocol [26] committing themselves to reduce their emission of greenhouse gases (CO_2, CH_4, N_2O, HFCs, PFCs and SF_6). Perfluorocompounds (PFCs) such as CF_4, hydrofluorocarbons (HFCs) like CHF_3, and SF_6 have considerable atmospheric lifetimes and are very efficient absorbers of infrared radiation resulting in a large global warming potential. These gases are extensively used for semiconductor manufacturing processes [27, 28]. Typically, the waste gas stream exhausting from semiconductor process tools that contains CF_4 or CHF_3 is diluted with vast quantities of air or N_2 and is either released into the atmosphere or thermally incinerated [27]. However, due to the thermal stability of PFCs or HFCs the incineration process is not completely effective, and thus some of these environmentally harmful compounds are emitted into the atmosphere. Recent studies indicate that atmospheric concentrations of CF_4 and CHF_3 increase at rates between 1.3 % (CF_4) and 5 % (CHF_3) per year [29]. In addition, the increased rate at which these gases are released by the semiconductor industry parallels the industry's significant growth rate. Another disadvantage of the thermal incineration method is that the waste gas streams from numerous tool sets are combined into a single waste gas stream prior to incineration [27]. This leads to numerous inefficiencies, because the incinerator must be permanently operated at parameters that give the best results for the bulk flow and not tuned to each individual stream. Abatement of the emissions at the exhaust of the individual semiconductor manufacturing tools appears to be closest to commercialization and to providing a cost-effective solution as an alternative tool to the presently used inefficient thermal incineration process tools.

Therefore, the decomposition of CF_4 and SF_6 has been investigated using the MSE plasma source incorporated into a reactor at high pressures from 100 mbar to atmospheric pressure. High pressure abatement tools are favored over low pressure tools, because the waste gas treatment at the end of the production line is only economical if an additional pump is not required (see Chapter 5) [30]. C. Geßner [23] started the CF_4 decomposition experiments with the MSE array mounted in a reactor module of 100 cm^3 volume (see Chapter 3.1) resulting in the presence of large dead volumes and low decomposition rates. In cooperation with the Institute for Microtechnology of the Technical University of Braunschweig a micro-reactor has been developed in order to improve the gas guidance and to exclude dead volumes resulting in high CF_4 decomposition rates. The micro-reactor consists of the MSE plasma source and a Foturan® glass reaction chamber, allowing direct view of the MSE and the plasma, respectively. Figure 1.2 shows a micro-reactor prototype (see Chapter 5 for details).

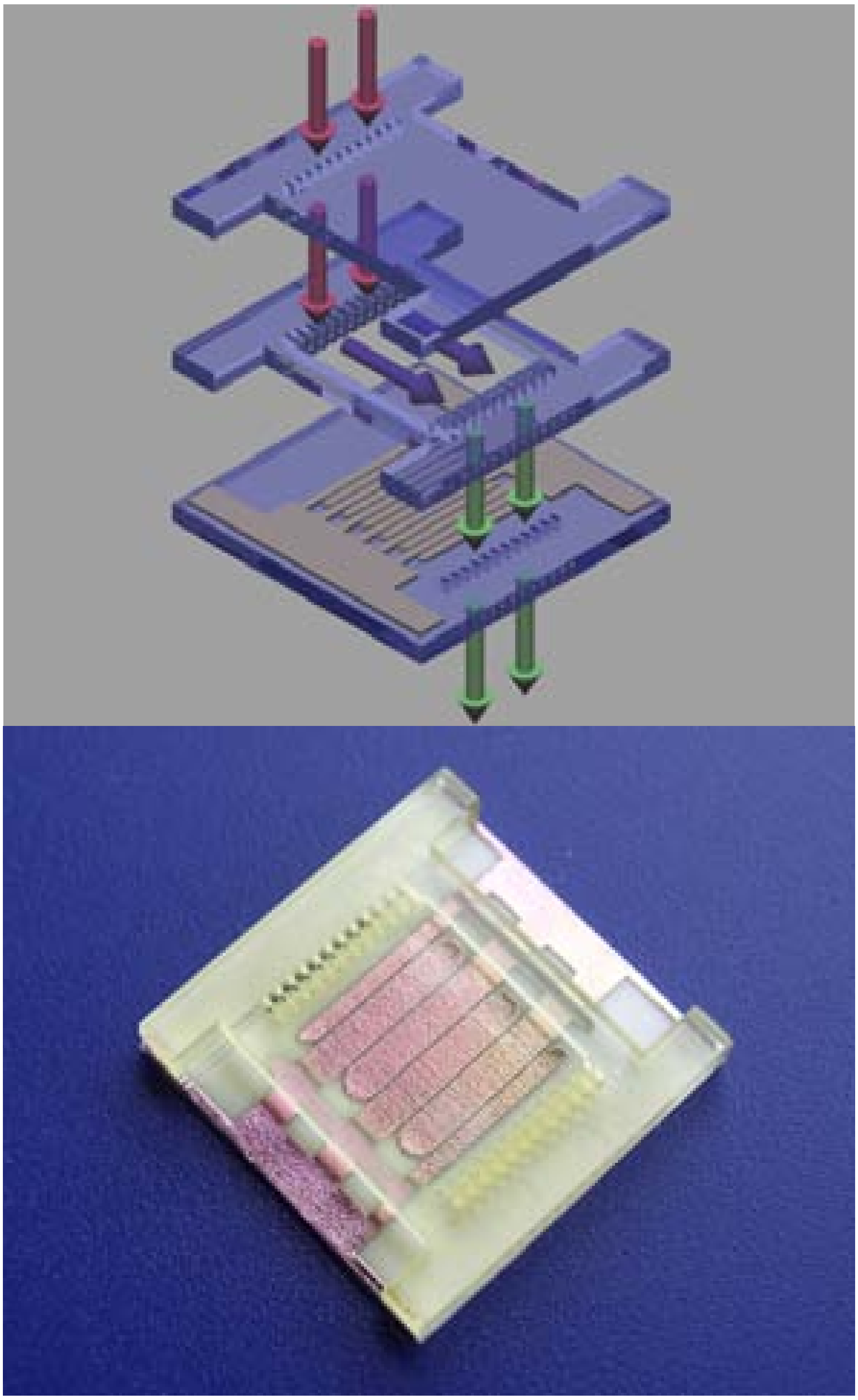

Figure 1.2. *Micro-reactor system* [31] *and prototype based on the MSE array as plasma source. The micro-reactor consists of the MSE base and a Foturan® glass reaction chamber, allowing direct view of the electrodes and the plasma, respectively (see Chapter 5 for details).*