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).

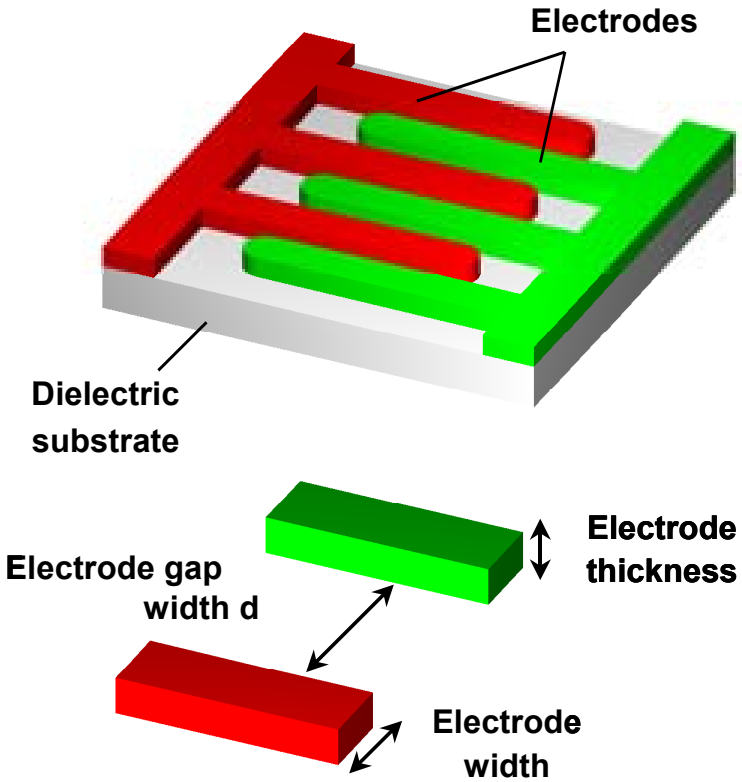

Figure 1.1. *Top: schematic view of a micro-structured electrode (MSE) array. The electrodes (comb-like capacitor structure) are arranged on an insulating substrate. Bottom: the characteristic electrode dimensions are electrode thickness and electrode width, and particularly, the electrode distance: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

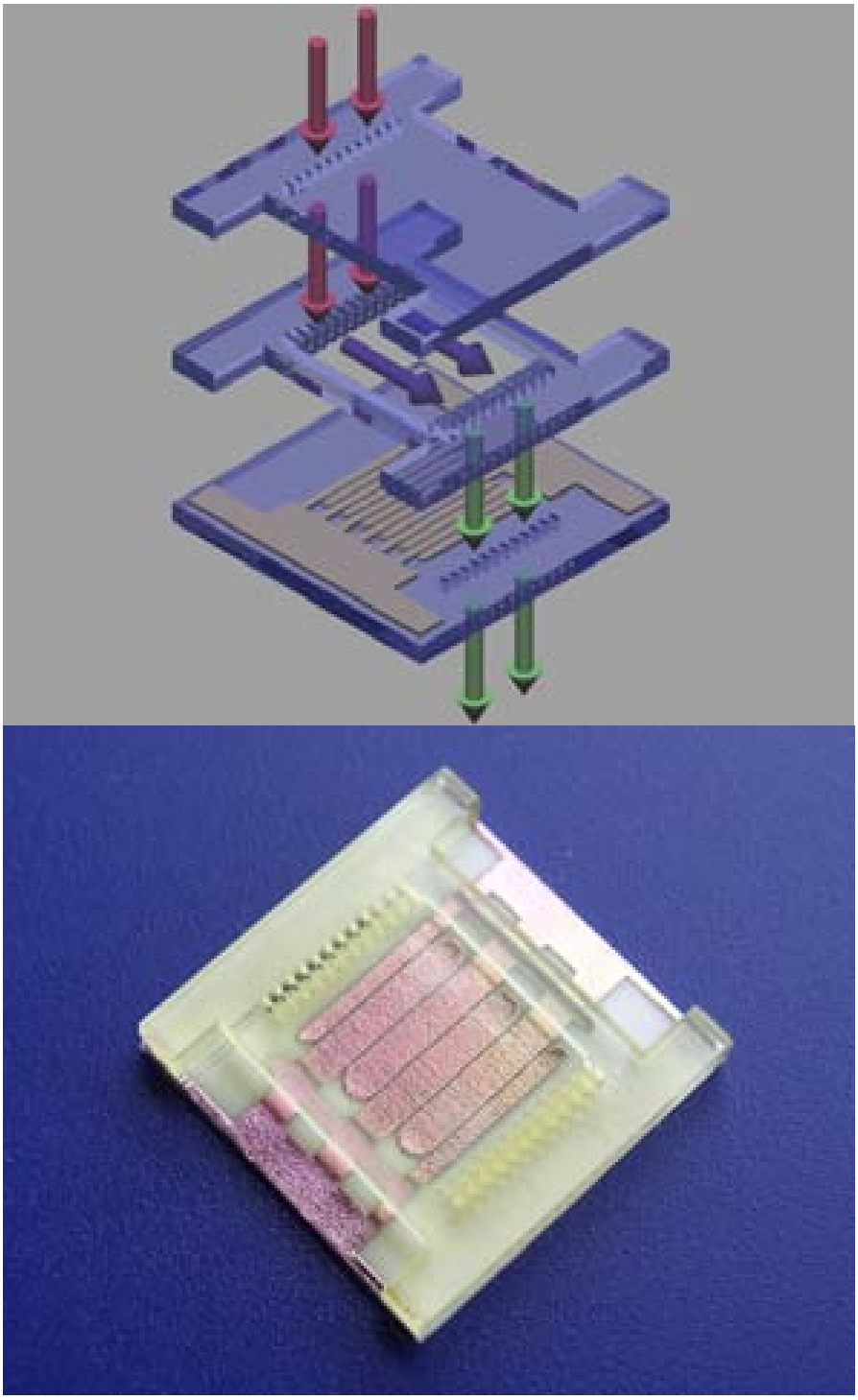

Figure 1.2. *Micro-reactor system* [31] *and prototype based on the MSE array as plasma source. The micro-reactor consists of the MSE base and a Foturan® glass reaction chamber, allowing direct view of the electrodes and the plasma, respectively (see Chapter 5 for details).*

1.2 Thesis Objective and Overview

As already introduced, MSE arrays are non-thermal atmospheric pressure plasma sources and act as the base of a micro-reactor system. The objective of this dissertation is to demonstrate that the MSE based micro-reactor is a powerful reactor module for plasma chemistry providing a modular scale-up for decentralized applications. In order to optimize the waste gas abatement rates, the influence of operation pressure, gas composition, electric power input, gas flow rate and other parameters on the decomposition performance has been investigated. An important aspect is the analysis of the decomposition gas mixture during plasma operation. The primary condition for high decomposition rates is a stable plasma operation, preferably at atmospheric pressure. Thus, the characterization of the MSE plasma is necessary to optimize the design of the MSE array and the plasma operation parameters, depending on the used pressure and gas type given by the application. Very important plasma parameters are the ignition parameters of the MSE driven RF plasma, electron density and voltage-current characteristic representing the operational range used by the applications.

Design, fabrication and testing of the MSE based micro-reactor developed and optimized for the decomposition of CF_4 was part of the project “Electrically controllable micro-reactors for the waste disposal of gaseous substances containing fluorine” (Verbundvorhaben “Elektrisch steuerbare Mikroreaktoren zur Abgasentsorgung fluorhaltiger Substanzen”) [32]. Within the scope of the project the Institute for Physical and Theoretical Chemistry cooperated with the Institute for Microtechnology and two industrial partners: the companies mikroglas chemtech GmbH (Mainz) and centrotherm Clean Solutions GmbH & Co. KG (Dresden).

The thesis content is mainly based on four publications which are integrated into the Chapters 4 and 5 concerned with the characterization of the MSE plasma source and its applications.

Chapter 2 (Theoretical Principals) introduces the important plasma parameters and derives the characteristic equations and formulas necessary to completely understand the results and discussions presented in Chapter 4. Particularly, the breakdown (ignition) regimes (e. g. DC Townsend breakdown regime) dominating the breakdown mechanism of the MSE driven RF discharge are explained in view of the given conditions (generator frequency, pressure, electrode gap width, gas type). As already mentioned, the Paschen similarity law is the basis of the realization of the MSE arrays, which corresponds directly to the DC Townsend breakdown theory.

Chapter 3 mainly describes the experiments for the electrical and thermal characterization of the MSE plasma. Beginning with the general experimental setup, the RF power supply system as well as temperature measurement and cooling are described in detail.

Chapter 4 consists of the two publications:

L. Baars-Hibbe, P. Sichler, C. Schrader, K.-H. Gericke, S. Büttgenbach, "Micro-structured electrode arrays: characterization of high frequency discharges at atmospheric pressure", *Plasma Processes and Polymers* **2005**, *2*, 174-182;

L. Baars-Hibbe, P. Sichler, C. Schrader, N. Lucas, K.-H. Gericke, S. Büttgenbach, "High frequency glow discharges at atmospheric pressure with micro-structured electrode arrays", *Journal of Physics D: Applied Physics* **2005**, *38*, 510-517.

The MSE plasma generated in different gases (Ne, He, Ar, N_2 and air) is characterized, especially, in view of the dominating breakdown mechanism. Characteristic discharge parameters such as electron density and voltage-current characteristic are determined and the results discussed.

Chapter 5 contains the applications of the MSE plasma source: particularly, the MSE array being the base of a micro-reactor. The first four major sections deal with the decomposition experiments of PFCs (particularly CF_4) and SF_6 (Chapters 5.1 to 5.4). Chapter 5.1 introduces the problem of decomposing the thermally stable fluorinated compounds and first successful low pressure approaches. The micro-reactor and its high pressure applications are introduced in Chapter 5.2 based on the publication:

L. Baars-Hibbe, P. Sichler, C. Schrader, C. Geßner, K.-H. Gericke, S. Büttgenbach, "Micro-structured electrode arrays: atmospheric pressure plasma processes and applications", *Surface and Coatings Technology* **2003**, *174-175*, 519-523.

The design and fabrication of the micro-reactor as well as of its scale-up – the multi-reactor – is described in the Chapters 5.2 and 5.3. Chapter 5.3 represents the publication:

P. Sichler, S. Büttgenbach, L. Baars-Hibbe, C. Schrader, K.-H. Gericke, "A micro plasma reactor for fluorinated waste gas treatment", *Chem. Engineering Journal* **2004**, *101*, 465-468.

In this section, the CF_4 decomposition results of the micro-reactor and the multi-reactor are compared with each other. The SF_6 decomposition results are discussed in Chapter 5.4, especially, in view of the ageing of the micro-reactor. In Chapter 5.5, the micro-reactor abatement and production of NO is compared with results already gained by the usage of MSE arrays mounted inside the reactor module (see Chapter 3.1.2) [21, 23]. Finally in

Chapter 5.6, the micro-reactor is evaluated recapitulatory as an alternative atmospheric pressure tool for the treatment of waste gases like CF_4 or NO.

All important results are summarized in Chapter 6 concluding with the development of new optimization approaches for a stable plasma operation at atmospheric pressure (particularly in N_2 and air).

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