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A micro plasma reactor for fluorinated waste gas treatment

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Abstract

A microreactor based on a micro-structured electrode (MSE) system is presented. With radio frequency electric power applied to the interdigitated, comb-like capacitor structure a homogeneous plasma is driven at atmospheric pressure with low ignition voltages due to small electrode gaps. The MSE is micromachined by plating nickel onto alumina ceramics. A micromachined Foturan® structure with inlet and outlet channels for the gas flow serves as a reaction chamber. The design of the reactor cell is arranged in a 4 × 4-array in a multireactor system. The performance of the reactor is modeled with computational fluid dynamics (CFD), used to improve the reactor design. Experiments show that CF_4 decomposition rates of over 70% can be achieved at atmospheric pressure.

Keywords: Microreactor; Atmospheric plasma; Fluorinated waste gas; Micro-structured electrode

1. Introduction

Up to now microreactors were mainly used because of their supreme surface to volume ratio in order to increase heat exchange and exposition effect of catalysts to media. The micro plasma reactor described in this paper makes use of very small electrode gaps between micro-structured electrodes (MSE) with an interdigitated arrangement as shown in Fig. 1 as (1). Advantages are low ignition voltages and an essentially homogeneous plasma at high pressure. The small gaps and planar geometry of the structure require micromachining via photolithography. The MSE are radio frequency (RF) driven and allow to generate large-area uniform glow discharges in He and Ne at pressures above 1500 mbar and in Ar and N_2 up to 1200 mbar. The discharges are non-thermal [1] and up to 500 mbar the plasma covers the whole electrode system. By breaking up bonds with high-energy electrons non-thermal plasma allows processing of reactions, which need more than 1000 °C in conventional thermal systems. Thus, a higher energy efficiency is given. One application which is investigated in this work is the decomposition of fluorinated waste gas as produced by semiconductor industry [2,3].

2. Design and micromachining of the reactor

Although MSE systems by itself can be used to drive chemical reactions [4], this reactor enhances effectiveness by thorough control of the gas flow. Due to the incorporation of fluorine chemistry the number of applicable materials is limited. Alumina substrates, electroplated nickel and Foturan® with an alumina coating were used as construction materials.

The MSE is plated 100 μm thick from a nickel bath of the sulphamate type [5]. Limited throwing power is partially compensated by current thiefs but also the important features are small gaps of 70 μm width, so no grinding is needed for planarization. The mold on the ceramic substrate is an 150 μm thick SU8 photoepoxy layer and is used because of its superior sidewall geometry compared to other resists applicable to standard UV-lithography [6]. After plating the removal of the SU8 is performed in acetone at 120 °C within 48 h and without any prior modification of the SU8 process limiting its performance. Possible residues are removed in a barrel etcher with a 300 W O_2 plasma with CF_4 admixture of 20%. An alumina layer is deposited on the top of the structure in order to protect the electrodes and to stabilize the plasma.

To find an optimized geometry of the structure the width and the gap of the electrodes are varied. Best results are achieved with gaps of 70 μm and widths of 1350 μm. Further improvements are in progress.

The micro plasma reactor as shown in Fig. 1 consists of the described MSE plasma source (1) on the ceramic substrate

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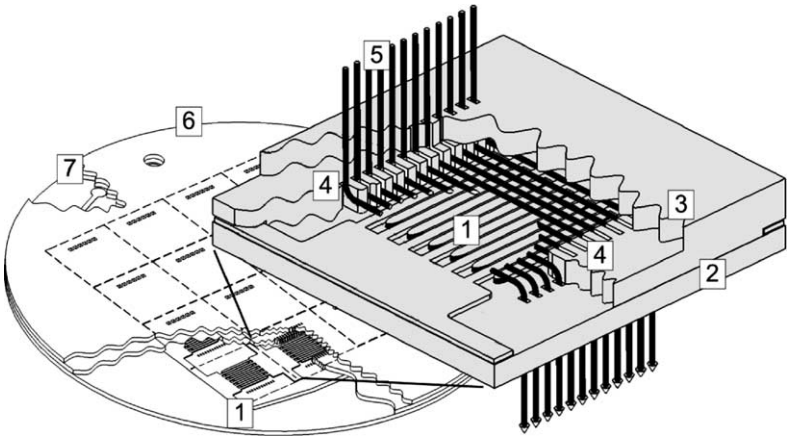

Fig. 1. Scheme of the multireactor, microreactor single cell and gas flow (numbered features explained in text).

(2) and a Foturan® [7] glass structure forming the reaction chamber (3).

The Foturan® structure allows direct view to the plasma and is protected against fluor etching by a sputtered alumina layer. Bonding is achieved by silicone glue at the borders of the cell. The inlet and the outlet of the reactor contains lamellae (4) in order to create a flow resistance. This design allows the gas flow (5) to be controlled by a pressure difference between upper and lower side. The base dimensions of the cell as shown in Fig. 1 are 15 mm × 15 mm with a height of 2.5 mm. The chamber size is 8.4 mm × 7.2 mm with a height of 1 mm resulting in a reactor volume of 60.5 mm^3. The single cell is investigated more detailed in [4]. The cell design is arranged in a 4 × 4-array in a multireactor (6). In this case RF power is supplied by two contact pads at the upper side (7).

3. Simulation

Simulation of the reactive gas flow in a single cell is performed with computational fluid dynamics (CFD) with the commercial package CFDRC-ACE+ from CFDRC Corporation, Huntsville. A 2D-model is used in order to limit computation time. The flow resistance of the lamellae at the front and end of the chamber is modeled by a narrow slit. The model predicts that a pressure difference of 40 Pa results in a gas flow of 50 sccm. The gas mixture for chemical reactions contains He with 5% CF_4, 5% H_2 and 5% O_2. Reaction equations are taken from [8] and instantaneous reactions of fluorine with H_2 are supplemented. As driving force for the reaction mechanism the mean value of the electron temperature (T_e) in the electrode gaps is set to a determined value whereas it is set to zero in the rest of the reactor model.

Fig. 2 shows the decomposition rate of CF_4 dependent on gas flow and applied value of T_e. At small gas flows of 0.4 sccm the predicted decomposition rate is higher than 90% even at a low T_e value of 10 eV. An increase of T_e shows little increase of the decomposition rate, but it is decreased strongly by an increase of gas flow. It is assumed that the contact time of the gas flow with the plasma is too small. The model shows that an enhancement of decomposition will be observed, if the chamber height is reduced.

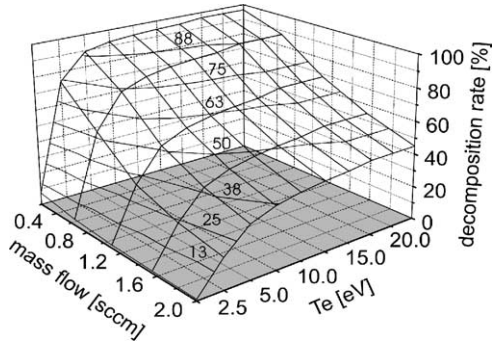

Fig. 2. Decomposition rates resulting from CFD simulation.

The simulation results cannot directly be compared with the decomposition experiments. The model uses different electron temperatures T_e as input and the reactor is powered by RF energy. Measurement of T_e with micro-sized double langmuir probes could not be done yet. However, simulation and experimental results can be fitted together so that every step in the RF power corresponds to one level of T_e in the simulation. After this fit deviations are less than 10%. This accuracy should be good enough to perform an optimization of the reactor geometry for a better decomposition performance in the future.

4. Experimental: decomposition of CF_4

Both the microreactor and the multireactor are installed onto a complex gas flow and water-cooling system inside a vacuum chamber. The entire experimental setup is described in detail elsewhere [1,4,9,10]. A gas flow rate between 1 and 200 sccm is set up by means of mass flow controllers. For online detection of the plasma product gases a differentially

pumped quadrupole mass spectrometer (Pfeiffer Vacuum QMS 200) is used. The discharges are generated using an RF power supply at 13.56 MHz (ENI ACG-6B) equipped with a matching network (ENI MW-10D). Between the matching network and the microreactor a special probe (ENI VI-Probe) is inserted in order to measure voltage, current and phase angle of the system.

It was already shown that in an MSE based microreactor the decomposition of CF_4 and NO are controllable by the applied generator power and the applied power density [4,11].

The multireactor allows to insert more efficiently power into the system than the microreactor. The CF_4 decomposition experiments in He at a pressure of 100 mbar are summarized in Table 1. A CF_4:H_2 ratio of 1:7 gives maximum CF_4 decomposition rates at a pressure of 100 mbar. The same gas mixture is used for the experiments with the microreactor and with the multireactor. Due to the parallel operation of 16 microreactors in the multireactor the mean residence time of the reaction gas mixture is 16 times longer than in one single microreactor. Thus, in order to achieve the same decomposition rate in the multireactor as in the microreactor less than one third of the power density applied in the microreactor is necessary. This optimization reduces the power strain on one single MSE and prolongs the lifetime of the microreactors.

As soon as the volumes of all 16 reaction chambers are entirely filled with plasma, an additional increase of the applied power density, even a doubling, results in a rate increase of only a few percent (from 83.3 to 89.5%). Thus, at a pressure of 100 mbar the decomposition of the remaining 10% of CF_4 is neither a problem of power insertion nor of dead volumes. In first experiments with N_2 as the carrier gas decomposition rates of 94% are achieved; the decomposition rate of CF_4 in N_2 is higher than in He, because N_2 acts as a reactant.

Table 2 summarizes the CF_4 decomposition experiments in He at atmospheric pressure. The optimal CF_4:H_2 ratio of 1:7 at a pressure of 100 mbar destabilizes the plasma at atmospheric pressure, as a result there is a plasma not between all electrode gaps and only low decomposition rates are achieved [4]. A reduction of the H_2 portion to 1 sccm stabilizes the plasma operation.

Table 1
CF_4 decomposition experiments in He at a pressure of 100 mbar: experimental parameters and decomposition rates of CF_4 dependent on the applied RF power density

Microreactor		Multireactor	
Power density ($W\,cm^{-2}$)	Decomposition rate (%)	Power density ($W\,cm^{-2}$)	Decomposition rate (%)
10.6	31.5	6.7	51.1
25.3	43.2	10.4	83.3
29.1	54.6	14.1	86.8
38.7	81.9	21.6	89.5

Pressure: 100 mbar. Microreactor—reactor volume: 60.5 mm^3; gas mixture: 1 sccm CF_4, 7 sccm H_2, 50 sccm He; mean residence time: 62.5 ms. Multireactor—reactor volume: $16 \times 60.5\,mm^3$; gas mixture: 1 sccm CF_4, 7 sccm H_2, 50 sccm He; mean residence time: 1.00 s.

Table 2
CF_4 decomposition experiments in He at a pressure of 1000 mbar: experimental parameters and decomposition rates of CF_4 dependent on the applied RF power density

Microreactor		Multireactor	
Power density ($W\,cm^{-2}$)	Decomposition rate (%)	Power density ($W\,cm^{-2}$)	Decomposition rate (%)
18.0	29.2	7.1	43.9
25.9	43.8	9.1	62.8
30.1	70.9	10.5	73.0

Pressure: 1000 mbar. Microreactor—reactor volume: 60.5 mm^3; gas mixture: 1 sccm CF_4, 1 sccm H_2, 50 sccm He; mean residence time: 69.8 ms. Multireactor—reactor volume: $16 \times 30.25\,mm^3$; gas mixture: 1 sccm CF_4, 1 sccm H_2, 100 sccm He; mean residence time: 285 ms.

With increasing pressure from 100 to 1000 mbar the plasma expansion decreases, until it is confined to the electrode gaps resulting in the presence of dead volumes in the reaction chambers at atmospheric pressure. Therefore, the reactor chamber height in the multireactor was reduced from 1 mm to 500 μm and the reactor volume halved that way. Additionally, a doubling of the He gas flow rate in comparison to the microreactor is necessary in order to get stable plasma operation conditions using the multireactor. Although the prolongation of the mean residence time is only fourfold in comparison to the experiments at 100 mbar, already one third of the applied microreactor power density results in a higher CF_4 decomposition rate than the maximum rate achieved with the microreactor.

During plasma operation an abatement of the fragments, radicals and molecules H (1), H_2 (2), H_2O (18), F (19), CF (31), O_2 (32), CF_2 (50) and CF_3 (69) is observed with the exception of the 1000 mbar He gas mixture where H_2O is produced. O_2 and H_2O are residual gases probably coming from the vacuum chamber walls. Both gases support the decomposition of CF_4, but an excess of O_2 or H_2O destabilizes the plasma and does not increase the rate.

The product distribution varies with pressure and carrier gas [4]. The following product molecules, fragments and radicals are detected: HF (20), CN (26), HCN (27), CO (28), NF (33), CO_2 (44), NO_2 (46), COF (47), NF_2 (52) and COF_2 (66). As expected [2,3] only small product molecules are produced. Most of the product molecules can be removed by passing the treated gas through a basic solution. The production of NF_3 (71), NO (30), N_2O_3 (76), N_2O_5 (108) and C_2F_6 (138) is not observed.

5. Conclusions

It is shown that MSE based microreactors can be used for processing in harsh environments including fluorine chemistry, high pressure and high electron energies. Effective

flow control can be applied by microstructures and shows great effect on decomposition efficiency. These properties give it capability to handle the abatement of fluorinated waste gas of semiconductor industry with high energy efficiency.

For the handling of large exhaust gas flows it is necessary to perform a numbering-up with a multireactor. In this paper the processing of the multireactor and first experimental results are shown. For a small semiconductor plant with 20 l/min of waste gas 25 multireactors are needed, if high gas flow rates per reactor cell are applied. A comparison of the necessary energy per volume shows, that approximately 50% of the energy of a combustion system is needed, promising some financial savings at this point of development.

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