Correlations between Gas Flow and Film Growth in Plasma Polymerization Processes

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Abstract: One of the challenges of plasma polymerization processes is the homogeneous coating of complex substrate geometries. This work shows how film homogeneity depends strongly on the transport of film forming species to the substrate surface and therefore on the monomer gas flow. It will be demonstrated how numerical gas flow simulations can be used to investigate and optimize the gas flow within the plasma chamber for different substrate geometries.

Keywords: plasma polymerization, film growth, gas flow simulation, residence time

1. Theoretical Approach

There is experimental evidence for the dependence of the deposition rate in plasma polymerization processes on the gas flow rate. It can be assumed that enhanced incorporation of film-forming species in the coating is not only related to the flux of film-forming species arriving at the substrate surface but also to longer residence times of the gas along the surface [1, 2].

To investigate the correlations between gas residence time and film growth the following modified Arrhenius relation for the flux of film-forming species Γ_p is considered, being largely independent of pressure which has been experimentally verified for different monomers [3]:

$$\Gamma_\mathrm{p} \sim F_\mathrm{m} \cdot \exp\left(-\frac{E_\mathrm{a}}{W/F_\mathrm{m}}\right) . \qquad (1)$$

F_m is the monomer flow rate, E_a the activation energy for the plasma chemical reactions and W the power input. The amount of species actually contributing to film growth depends on the sticking probability s. The flux of deposited particles Γ_dep can therefore be related to the overall flux of film-forming material via s and is found to be proportional to the mass deposition rate R_m [3]:

$$\Gamma_\mathrm{dep} \sim s \cdot \Gamma_\mathrm{p} = R_\mathrm{m} . \qquad (2)$$

The flux of activated plasma species as well as the probability for a reaction to take place at the substrate surface seem to depend strongly on the residence time [4, 5, 6]. Therefore it can be assumed that the sticking probability (for sticking coefficients <1) depends on the residence time τ_surf:

$$s = s(\tau_\mathrm{surf}) . \qquad (3)$$

To further investigate this relation experiments are carried out in order to determine deposition rates for plasma polymerization processes. By keeping W/F_m and plasma volume constant, i.e. the exponential part in equation (1), the flow rate can be directly correlated with sticking probability and mass deposition rate. On the other hand, numerical gas flow simulations are applied to calculate flow velocities and residence times for the monomer flow rates used in the experiment.

The comparison of experimental and numerical results then gives insight into the influence of gas flow properties on film growth.

2. Experimental Setup

The coating experiments are conducted with a symmetric, capacitively coupled plasma reactor (Fig. 1). The device has a diameter of 30 cm and consists of two plane parallel electrodes confining a homogeneous plasma which is operated at low pressure conditions. The lower electrode is RF-driven (13.56 MHz).

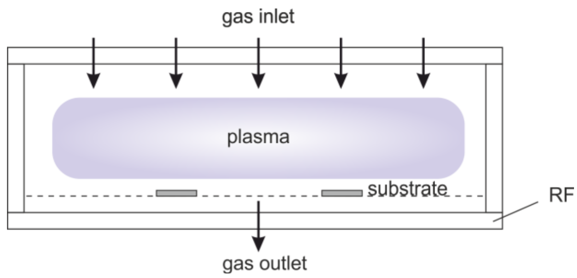

Fig. 1. Capacitively coupled plasma reactor used for film deposition. The symmetrical setup of the reactor and the uniform gas supply lead to a homogeneous plasma.

A mixture of ethylene (C_2H_4) and ammonia (NH_3) is chosen as precursor gas. The gas is uniformly distributed through symmetrically aligned gas inlets integrated in the upper electrode and pumped through the centre of the lower electrode which is covered by a grid.

The ratio between input power and gas flow rate is kept constant for all deposition conditions. Gas flow rate and pressure, both of which affect gas flow velocity, are varied systematically. In this way the effect of changing residence time at the surface can be investigated, while the flux of film-forming species only depends on F_m.

In a first step films were deposited onto flat substrates (1 x 1 cm). The findings will later help to investigate plasma polymerization on more complex, three-dimensional geometries. After the deposition film thickness is measured using profilometry. In addition the samples are weighed to obtain mass deposition rates.

3. Numerical Model

For the modelling and simulation of the gas flow the finite element software Comsol Multiphysics® is used. Considering the dimensions of the reactor and the applied pressure range (0.01 – 0.3 mbar) the gas flow can be treated as a continuum flow. Therefore Navier-Stokes equations are chosen. Due to high Reynolds numbers turbulence effects have to be taken into account. This is done by using the *k*-*ε* turbulence model which adds two additional transport equations for turbulence kinetic energy *k* and dissipation rate of turbulence energy *ε*.

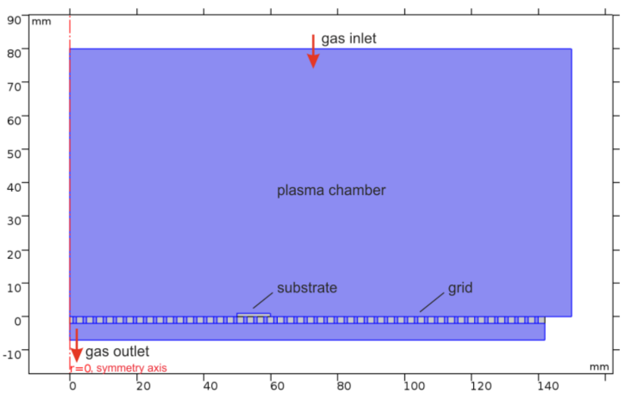

Fig. 2. Model geometry used for the simulation of the gas flow. It represents a two-dimensional, axially symmetric cut through the plasma reactor.

A two-dimensional, axially symmetric model geometry is used which represents a cut through the cylindrical plasma reactor (Fig. 2). To represent the substrate a flat and a cup-shaped geometry are chosen. The substrates are placed on the grid which is covering the gas outlet.

As in the experiment gas flow rate and pressure are varied. The resulting velocity profiles provide information about the spatial distribution of gas residence time in the reactor volume and along the substrate surface.

4. Results

The dependence of the experimentally determined mass deposition rate on gas pressure for a gas flow rate of 14 sccm (7/7 sccm C_2H_4/NH_3) and a power input of 70 W is shown in Fig. 3 yielding a constant flux of film-forming species for all conditions examined.

Since pressure is inversely proportional to gas flow velocity and thus directly proportional to the residence time of the gas, the results confirm the hypothesis that an increase in residence time leads to faster film growth. This is a first, strong indication to verify the assumptions made about the correlations between gas flow properties and deposition rate.

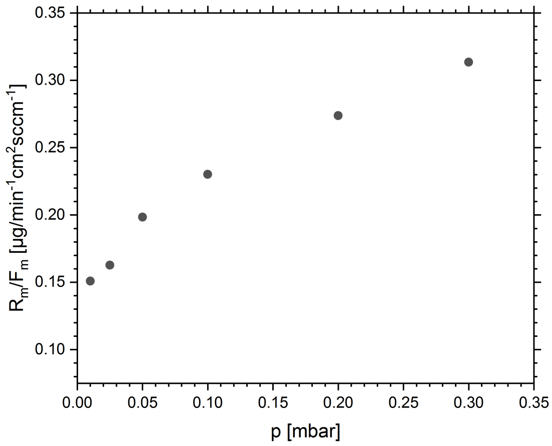

Fig. 3. Experimental results: mass deposition rate, normalized on the gas flow, increases with gas pressure. A gas flow rate of 14 sccm (7/7 sccm C_2H_4/NH_3) and a power input of 70 W were used.

First simulation results of the gas flow (gas flow rate: 14 sccm, pressure: 0.01 mbar) in the presented plasma reactor are shown in Fig. 4 and Fig. 5. The comparison of the velocity profiles around a flat and a cup-shaped geometry illustrates the strong influence of the form of the substrate on the gas flow.

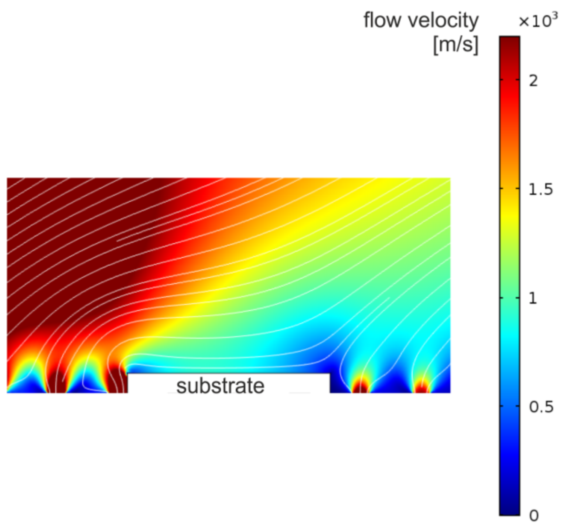

Fig. 4. Simulation result: the gas flow velocity close to a flat substrate (placed on the grid) varies along the substrate surface. Gas flow rate: 14 sccm, pressure: 0.01 mbar.

By looking at the velocity profile around the flat substrate (Fig. 4) it becomes evident that flow velocity and therefore residence time cannot be considered to be constant, not even along a short substrate surface (in the present case the substrate has a length of 1 cm).

Taking the preliminary experimental results into account, which show evidence that there is a close relation between residence time of the gas and the film growth rate, it can be concluded that inhomogeneities in film thickness can arise from such non-uniform gas flow conditions.

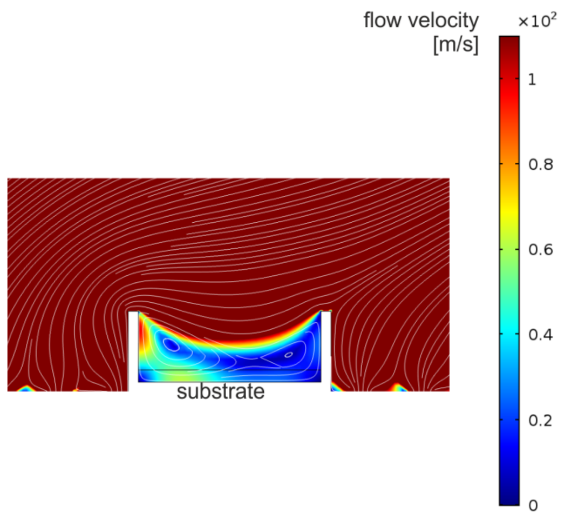

Fig. 5. Simulation result: the gas flow velocity close to a cup-shaped substrate (placed on the grid) varies along the substrate surface. Stagnation points may prevent the gas from being exchanged sufficiently. Gas flow rate: 14 sccm, pressure: 0.01 mbar.

The flow pattern for the cup-shaped substrate (Fig. 5) shows areas of stagnation inside the cup with low flow velocities, especially in the corners of the geometry. This can be assumed to make it more difficult to obtain the same coating conditions as in the areas with higher velocity. In addition to the factor of changing residence time it also has to be taken into account that the monomer gas may not be exchanged sufficiently in some areas in order to provide a uniform coating.

5. Conclusion

A theoretical approach has been presented which relates film growth in plasma polymerization processes to prevalent gas flow conditions. A first qualitative comparison of experimentally obtained deposition rates and gas flow properties support the assumed correlations.

The experimental results show that deposition rate increases for longer residence times of the gas at the substrate surface. The findings of the numerical gas flow simulation give insight into the spatial distribution of gas flow velocity and reveal that residence time varies significantly along the surface of a flat and a cup-shaped substrate. Following the proposed hypothesis it can be concluded that this can cause film inhomogeneities.

Furthermore, the simulations showed evidence that for more complex substrate geometries the effect of gas stagnation becomes important. It has to be taken into account that this may lead to an insufficient supply of fresh monomer gas in some areas, equivalent to a local reduction of Γ_p .

The results show that for further experiments it is crucial to not only measure an overall deposition rate for a substrate but that it is advantageous to determine the spatial distribution of the film thickness. Thus differences in residence time and gas transport along the surface, which can be accessed by gas flow simulation, can directly be related to the assumed variation in film thickness.

A systematic comparison of the results will then help to quantify the presented correlations and to determine sticking probabilities.

6. References

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