Simulation of a Multi-Component Transport Model for the Chemical Reaction of a CVD-Process

J. Geiser, R. Röhle

***Abstract*—**In this paper we present discretization and decomposition methods for a multi-component transport model of a chemical vapor deposition (CVD) process. CVD processes are used to manufacture deposition layers or bulk materials. In our transport model we simulate the deposition of thin layers. The microscopic model is based on the heavy particles, which are derived by approximately solving a linearized multicomponent Boltzmann equation. For the drift-process of the particles we propose diffusion-reaction equations as well as for the effects of heat conduction. We concentrate on solving the diffusion-reaction equation with analytical and numerical methods. For the chemical processes, modelled with reaction equations, we propose decomposition methods and decouple the multi-component models to simpler systems of differential equations. In the numerical experiments we present the computational results of our proposed models.

***Keywords*—**Chemical reactions, chemical vapor deposition, convection-diffusion-reaction equations, decomposition methods, multi-component transport.

AMS subject classifications: 35K57, 76R50, 74S20, 65M12.

I. INTRODUCTION

WE are motivated to study the deposition of a CVD process with low-temperature and low-pressure plasma. In the last years, due to the research in producing high temperature films by depositing of low pressure processes the interest on such apparatuses has increased. We present such a model for low temperature and low pressure plasma, that can be used to implant or deposit thin layers of important materials. The applications are used in the production of so called metallic bipolar plates, which are used in polymer electrolyte fuel cells (PEFC), see [2].

Our apparatus is based on a plasma, which is modeled by a Boltzmann equation for the heavy particles and for their drift we use a classical diffusion equation, see [22]. For the simplification we neglect the electron modeling, because of their sufficient small influence.

Further we concentrate on modelling the reaction-processes in the CVD apparatus, which can be done with coupled reaction equations.

The numerical approximation is done by applying semi-analytical methods or finite difference methods of second order in space and time. For the effective computations we propose the Waveform-relaxation method as a decomposition method for the multi-species reaction equations.

The paper is outlined as follows.

In section 2 we present our mathematical model and a possible reduced model for the further approximations. In section 3 we discuss the time and spatial discretization methods. Further in section 4, we propose the Waveform-relaxation method for decoupling the complicate equations to reduce the amount of computational work. The numerical experiments are given in Section 5. In the contents, that are given in Section 6, we summarize our results.

II. MATHEMATICAL MODEL

In the following a model is presented due to the motivation in [22] and [14].

The modeling is considered for the chemical reactions in the plasma reactor.

The simulation of the thin-film deposition can be done with a reaction equation combined with a diffusion equation, see [20].

We will concentrate on the reaction equations, which are given as

$$\partial_t u_1 + v_1 \nabla u_1 = -\lambda_1 u_1 + \lambda_2 u_2 + \ldots + \lambda_m u_m \text{ in } \Omega \times (0,T), \quad (1)$$
$$\vdots$$
$$\partial_t u_m + v_m \nabla u_m = \lambda_1 u_1 + \lambda_2 u_2 + \ldots - \lambda_m u_m \text{ in } \Omega \times (0,T), \quad (2)$$
$$u(x,0) = \left(c_0(x),\ldots,c_m(x)\right)^t \in \Omega,$$

where the unknowns are given as $u_1 = u_1(x,t)$ till $u_m = u_m(x,t)$ in $(0,T) \subset \mathbb{R}^+$.

m is the number of species, e.g. reactants, heavy particles, etc.. The interactions are chemical reactions between the species and given as λ_1 till λ_m. We assume the same densities c_0 till c_m of the species as initial condition. For the boundary conditions we assume Neumann- or Dirichlet boundaries.

A. Large Knudsen Numbers

The model assumes that the heavy particles can be described with a fluid dynamical model, where the elastic collision define the dynamics and few inelastic collisions are, among other reasons, responsible for the chemical reactions.

To describe the individual mass densities, as well as the global momentum and the global energy as the dynamical conservation quantities of the system, corresponding conservation equations are derived from Boltzmann equations.

J. Geiser is scientific researcher with the Humboldt University of Berlin, Germany, Unter den Linden 6, D – 10099 Berlin (phone: 030 2093 5451; fax: 030 2093 5859, e-mail: geiser@mathematik.hu-berlin.de).

R. Röhle is student researcher with the Humboldt University of Berlin, Unter de Linden 6, D – 10099 Berlin (e-mail: roehle@mathematik.hu-berlin.de)

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The individual character of each species is considered by mass-conservation equations and the so called difference equations.

The Boltzmann equations for the heavy particles (Ions and Neutral elements) are given as

$$\frac{\partial}{\partial t} n_s + \frac{\partial}{\partial r} \cdot \left(n_s u + n_s c_s \right) = Q_n^{(s)},$$

$$\frac{\partial}{\partial t} \rho u + \frac{\partial}{\partial r} \cdot \left(\rho u u + nT \underline{\underline{I}} - \underline{\underline{\tau}}^* \right) = \sum_{s=1}^{N} q_s n_s \langle E \rangle,$$

$$\frac{\partial}{\partial t} \varepsilon_{tot}^* + \frac{\partial}{\partial r} \cdot \left(\varepsilon_{tot}^* u + q^* + nTu - \underline{\underline{\tau}}^* \cdot u \right) =$$
$$\sum_{s=1}^{n} q_s n_s \left(u + c_s \right) \cdot \langle E \rangle - Q_{\varepsilon,inel}^{(e)}.$$

where ρ is the mass density, u is the velocity and T is the temperature of the ions.

Further the production terms $Q_n^{(s)} = \sum_r a_{sign} k_{\alpha,r} n_\alpha n_r$, where the rate coefficients are $k_{\alpha,r}$.

The drift diffusion for the heavy particles are in the following fluxes. The dissipative fluxes of the impulse and energy balance are linear combinations of generalized forces

$$q^* = \lambda_E \langle E \rangle - \lambda \frac{\partial}{\partial r} T - \sum_{s=1}^{N} \sum_{\alpha}^{N} \lambda_n^{(\alpha,s)} \frac{1}{n_s} \frac{\partial}{\partial r} n_\alpha,$$

$$\underline{\underline{\tau}}^* = -\eta \left(\frac{\partial}{\partial r} u + \left(\frac{\partial}{\partial r} u \right)^T - \frac{2}{3} \left(\frac{\partial}{\partial r} \cdot u \right) \underline{\underline{I}} \right),$$

$$\varepsilon_{tot}^* = \sum_{s=1}^{N} \frac{1}{2} \rho_s c_s^2 + \frac{1}{2} \rho u^2 + \frac{3}{2} nT.$$

The diffusion of the species is underlying to the given plasma and described by the following equations

$$\frac{\partial}{\partial t} n_s + \frac{\partial}{\partial r} \cdot \left(n_s u + n_s c_s \right) = Q_n^{(s)},$$

$$c_s = \mu_s \langle E \rangle - d_T^{(s)} \frac{\partial}{\partial r} T - \sum_{\alpha=1}^{N} D_n^{(\alpha,s)} \frac{1}{n_s} \frac{\partial}{\partial r} n_\alpha.$$

The densities of the species are dynamical values and the species transport and mass transport are underlying to the following constraint conditions

$$\sum_s m_s n_s = \rho,$$

$$\sum_s n_s m_s c_s = 0.$$

Fieldmodel

The plasma transport equations are maxwell equations and are coupled with a field. They are given as

$$\frac{1}{\mu_0} \nabla \times B_{dyn} = -e n_e u_e + \tilde{j}_{ext},$$

$$\nabla \cdot B_{dyn} = 0,$$

$$\nabla \times E = -\frac{\partial}{\partial t} B_{dyn}.$$

B. Simplified model for large Knudsen Numbers

For the numerical analysis and for the computational results, we reduce the complex model and derive a system of coupled Boltzmann and Diffusion equations.

We do the following assumptions:

$$q^* = -\lambda \frac{\partial}{\partial r} T,$$

$$\underline{\underline{\tau}}^* = 0,$$

$$Q_{\varepsilon,inel}^{(e)} = \text{const}$$

and we obtain the system of equations:

$$\frac{\partial}{\partial t} \rho + \frac{\partial}{\partial r} \cdot \left(\rho u \right) = 0,$$

$$\frac{\partial}{\partial t} \rho u + \frac{\partial}{\partial r} \cdot \left(\rho u u + nT \underline{\underline{I}} \right) = \sum_{s=1}^{N} q_s n_s \langle E \rangle,$$

$$\frac{\partial}{\partial t} \frac{3}{2} nT + \frac{\partial}{\partial r} \cdot \left(\frac{3}{2} nTu + \lambda \frac{\partial}{\partial r} T + nTu \right) =$$
$$\sum_{s=1}^{N} q_s n_s \left(u + c_s \right) \cdot \langle E \rangle - Q_{\varepsilon,inel}^{(e)}.$$

Remark 1. We obtain three coupled equations for the density, velocity and the temperature of the plasma. The equations are strong coupled and a decomposition can be done in the discretized form.

C. Chemical Reactions

For the application of the material balance to model the CVD apparatus, the chemical reactions are important to understand the chemical kinetics of the system, see [20].

We discuss the influence of concentration on kinetics and especially to gross reaction types.

To describe our chemical reactions, the following types are necessary:
– Autocatalytic Reactions
– Consecutive Reactions
– Parallel Reactions
– Complex Reactions

In the models we achieve the following terms with the reaction parts:

1.) Autocatalytic Reactions: Here we have the following reaction: $A \xrightarrow{k} P$, where A and P are the reactants.

For the reaction rates, we obtain the term: $R_A = -k c_A c_P$, so that our differential equation is given as

$$\frac{\partial c_A}{\partial t} = -k c_A c_P \tag{3}$$

where c_A, c_P are the concentration of each species.

2.) Consecutive Reactions: Here we have the following reactions: $A \xrightarrow{k_1} B$ and $B \xrightarrow{k_2} C$, where A, B and C are the reactants.

For the reaction rates, we obtain the terms: $R_A = -k_1 c_A$, $R_B = k_1 c_A - k_2 c_B$ and $R_C = k_2 c_B$. The differential equation is given as

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$$\frac{\partial c_A}{\partial t} = -k_1 c_A, \tag{4}$$

$$\frac{\partial c_B}{\partial t} = k_1 c_A - k_2 c_B, \tag{5}$$

$$\frac{\partial c_C}{\partial t} = k_2 c_B, \tag{6}$$

where c_A, c_B and c_C are the concentration of each species.

3.) Parallel Reactions: Here we have the following types: $A \xrightarrow{k_1} P$, $A \xrightarrow{k_2} X$, where A , P and X are the reactants. For the reaction rates, we obtain the terms: $R_A = -(k_1 + k_2) c_A$, $R_P = k_1 c_A$ and $R_X = k_2 c_A$. The derived differential equations are given as:

$$\frac{\partial c_A}{\partial t} = -(k_1 + k_2) c_A, \tag{7}$$

$$\frac{\partial c_P}{\partial t} = k_1 c_A, \tag{8}$$

$$\frac{\partial c_X}{\partial t} = k_2 c_A, \tag{9}$$

where c_A , c_P and c_X are the concentrations of each species.

4.) Complex Reactions: We deal with the following examples: $A \xrightarrow{k_1} P \xrightarrow{k_2} Q$ with $A \xrightarrow{k_3} X$, $P \xrightarrow{k_4} Y$ and $A + B \xrightarrow{k_1} P$ with $A + P \xrightarrow{k_2} X$. Here we have combinations of parallel and consecutive reactions.

The differential equations can be solved analytically or numerically. We propose the Waveform-relaxation method, see [17], [23], because of its decomposition idea to simpler parts. We have also taken into account the more difficult part with adding the diffusion processes to the kinetic model. Therefore we can deal with the operator-splitting and decouple the transport and reaction equations, see [9].

III. Time- and Spatial Discretization methods

In the following we describe the time and spatial discretization methods. We consider the following ordinary linear differential equation:

$$\partial_t c(t) = A c(t) + B c(t),$$

where the initial-conditions are given as $c^n = c(t^n)$. The operators A and B are assumed to be spatial discretised, e.g. convection or reaction operators.

A. Time Discretization methods

For the multiple species reaction models we need to investigate numerical methods for solving the equations. Such time-dependent equations we treat with Runge-Kutta and Backward Differential Formula (BDF) and Implicit-Explicit (IMEX) methods.

Runge-Kutta, BDF and IMEX methods

For the time-discretization of our diffusion-reaction equations we taken into account the stiff and non-stiff parts of the equation-parts. Because of the nonstiff diffusion part and the stiff reaction part, we propose the combination of explicit and implicit methods, see [3] and [1].

Therefore we propose the Runge-Kutta and BDF methods as adapted timediscretization methods to reach higher-order results.

For the time-discretization we use the following higher-order discretization methods.

Runge-Kutta method

We use the implicit trapezoidal rule:

$$
\begin{array}{c|cc}
0 & & \\
1 & \frac{1}{2} & \frac{1}{2} \\
\hline
& \frac{1}{2} & \frac{1}{2}
\end{array}
\tag{10}
$$

Furthermore we use the following Gauss-Runge-Kutta method:

$$
\begin{array}{c|cc}
\frac{1}{2} - \frac{\sqrt{3}}{6} & \frac{1}{4} & \frac{1}{4} - \frac{\sqrt{3}}{6} \\
\frac{1}{2} + \frac{\sqrt{3}}{6} & \frac{1}{4} + \frac{\sqrt{3}}{6} & \frac{1}{4} \\
\hline
& \frac{1}{2} & \frac{1}{2}
\end{array}
\tag{11}
$$

To use these Runge-Kutta methods with the Waveform-Relaxation method, we have to take into account that we solve equations of the form $\partial_t u_i = A u_i + b$ in each iteration step, where $b = B u_{i-1}$ is the right hand side and given at the solution u_{i-1} .

For the implicit trapezoidal rule this is no problem, because we do not need the values at any sub-points. However, for the Gauss method we need to know the values of b at the sub-points $t_0 + c_1 h$ and $t_0 + c_2 h$ with $c = \left(\frac{1}{2} - \frac{\sqrt{3}}{6}, \frac{1}{2} + \frac{\sqrt{3}}{6} \right)^T$.

Therefore we must interpolate b . On that account we choose the cubic spline functions.

Numerical experiments show that this works properly with non-stiff problems, but not very well with stiff problems.

B. BDF method

Because the higher-order Gauss-Runge-Kutta method combined with cubic spline interpolation does not work properly with stiff problems, we use the following BDF method of order three, which does not need any sub-points and therefore no interpolation.

The BDF3 method is defined by

$$\frac{1}{k}\left(\frac{11}{6} u^{n+3} - 3 u^{n+2} + \frac{3}{2} u^{n+1} - \frac{1}{3} u^n \right) = A\left(u^{n+3}\right) + B\left(u^{n+3}\right) \tag{12}$$

For the pre-stepping, i.e. to obtain u_n , u_{n+1} , we use the implicit trapezoidal rule (10).

Implicit-explicit methods

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The IMEX schemes have been widely used for time integration of spatial discretized partial differential equations of the diffusion-convection type. These methods are applied to decouple the implicit and explicit terms. Treating the convection-diffusion equation for example, one can use the explicit part for the convection and the implicit part for the diffusion term. In our application we divide between the stiff and non-stiff term, so we apply the implicit part for the stiff operators and the explicit part for the non-stiff operators.

FSRK method
We propose the A-stable fractional-stepping Runge-Kutta (FSRK) scheme, see [3], of first and second order for our applications. The tableau in the Butcher form is given as

1	1				0			
1	1	0			0	1		
$\frac{4}{9}$	$-\frac{88}{45}$	0	$\frac{12}{5}$	0	0	$\frac{5}{9}$	0	
$\frac{1}{3}$	$-\frac{407}{75}$	0	$-\frac{144}{25}$	0	0	$-\frac{31}{15}$	0	$\frac{12}{5}$
order 1	1	0	0	0	0	1	0	0
order 2	$\frac{1}{10}$	0	$\frac{9}{10}$	0	0	$\frac{1}{4}$	0	$\frac{3}{4}$

$$(13)$$

To obtain second-order convergence in numerical examples it is important to split the operator in the right way as we will show later.

SBDF Method
We use the following stiff backward differential formula (SBDF) method, which is a modification of the third-order backward differential formula (BDF3) method.
As pre-stepping method we again use the implicit trapezoidal rule.

$$\frac{1}{k}\left(\frac{11}{6}u^{n+1} - 3u^n + \frac{3}{2}u^{n-1} - \frac{1}{3}u^{n-2}\right) =$$
$$3A(u^n) - 3A(u^{n-1}) + A(u^{n-2}) + B(u^{n+1}). \quad (14)$$

Again it is important to split the operator in the right way.

C. Spatial Discretization methods
We discretize the diffusion-dispersion-equation with implicit time-discretization and finite-volume method for the following equation

$$\partial_t Rc - \nabla \cdot (D\nabla c) = 0 \quad (15)$$

where $c = c(x,t)$ with $x \in \Omega$ and $t \geq 0$. The diffusion-dispersion-tensor $D = D(x,v)$ is given by the Scheidegger-approach, cf. [21]. The velocity is given as v. The retardation-factor is $R > 0.0$.

The boundary-values are denoted by $n \cdot D\nabla c(c,t) = 0$, where $x \in \Gamma = \partial\Omega$ is the boundary, cf. [10]. The initial conditions are given by $c(x,0) = c_0(x)$.

We integrate the equation (17) over space and time and derive

$$\int_{\Omega_j}\int_{t^n}^{t^{n+1}} \partial_t R(c)\,dtdx = \int_{\Omega_j}\int_{t^n}^{t^{n+1}} \nabla \cdot (D\nabla c)\,dtdx. \quad (16)$$

The time-integration is done by the backward-Euler method and the diffusiondispersion term is lumped, cf. [12]

$$\int_{\Omega_j}\left(R(c^{n+1}) - R(c^n)\right)dx = \tau^n \int_{\Omega_j} \nabla \cdot (D\nabla c^{n+1})\,dx, \quad (17)$$

The equation (17) is discretized over the space with respect of using the Greensformula.

$$\int_{\Omega_j}\left(R(c^{n+1}) - R(c^n)\right)dx = \tau^n \int_{\Gamma_j} Dn \cdot \nabla c^{n+1}\,d\gamma, \quad (18)$$

where Γ_j is the boundary of the finite-volume cell Ω_j. We use the approximation in space, cf. [12].

The spatial-integration for (18) is done by the mid-point rule over the finite boundaries and given as

$$V_j R(c_j^{n+1}) - V_j R(c_j^n) = \tau^n \sum_{e\in\Lambda_j}\sum_{k\in\Lambda_j^e} \left|\Gamma_{jk}^e\right| n_{jk}^e \cdot D_{jk}^e \nabla c_{jk}^{e,n+1} \quad (19)$$

where $\left|\Gamma_{jk}^e\right|$ is the length of the boundary-element Γ_{jk}^e. The gradients are calculated with the piecewise finite-element-function ϕ_l and we obtain

$$\nabla c_{jk}^{e,n+1} = \sum_{l\in\Lambda^e} c_l^{n+1}\nabla\phi_l(x_{jk}^e). \quad (20)$$

We get with the difference-notation for the neighbor-point j in the following equation, cf. [10]

$$V_j R(c_j^{n+1}) - V_j R(c_j^n) =$$

$$\tau^n \sum_{e\in\Lambda_j}\sum_{l\in\Lambda^e\backslash\{j\}}\left(\sum_{k\in\Lambda_j^e}\left|\Gamma_{jk}^e\right| n_{jk}^e \cdot D_{jk}^e \nabla\phi_l(x_{jk}^e)\right)(c_j^{n+1} - n_l^{n+1}), \quad (21)$$

where $j = 1,\dots,m$.

IV. DECOMPOSITION METHODS

In the following we present the different decomposition methods, with respect to our application.

A. Operator Splitting method
The following splitting methods we propose to decomposition in different operators. Our methods are based on sequential splitting method, see [8].
We consider the following ordinary linear differential equation:

$$\partial_t c(t) = Ac(t) + Bc(t), \quad (22)$$

where the initial-conditions are given as $c^n = c(t^n)$. The operators A and B are assumed to be bounded linear operators in the Banach-space X with $A, B : X \to X$. In applications the operators correspond to the physical operators, e.g. the convection- and the diffusion-operator.

The operator-splitting method is introduced as a method which solves two equation-parts sequentially, with respect to initial conditions. The method is given as following

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$$\frac{\partial c^*(t)}{\partial t} = Ac^*(t), \quad \text{with } c^*(t^n) = c^n, \tag{23}$$

$$\frac{\partial c^{**}(t)}{\partial t} = Ac^{**}(t), \quad \text{with } c^{**}(t^n) = c(t^{n+1}).$$

where the time-step is given as $\tau^n = t^{n+1} - t^n$. The solution of the equation (22) is $c^{n+1} = c^{**}(t^{n+1})$.

The splitting-error of the method is derived with Taylor-expansion, cf. [12]. We obtain the global error as

$$\rho_n = \frac{1}{\tau}\left(\exp\left(\tau^n(A+B)\right) - \exp\left(\tau^n B\right)\exp\left(\tau^n A\right)\right)c(t^n) =$$

$$\frac{1}{2}\tau^n[A,B]c(t^n) + O\left((\tau^n)^2\right), \tag{24}$$

where $[A,B] = AB - BA$ is the commutator of A and B. We get an error $O(\tau^n)$ if the operators A and B do not commutate, otherwise the method is exact.

B. The Waveform-Relaxation Method

A method to solve large coupled differential equations is the Waveform-Relaxation scheme.

The iterative method was discussed in [23], [17] and [15]. For the method, there exist Gauss- or Jacobian schemes to decouple at least the schemes more or less effective.

We deal with the following ordinary differential equation or assume a semidiscretised partial differential equation:

$$u_t = f(u,t), \text{ in } (0,T),$$

$$u(0) = c_0,$$

where $u = (u_1, u_2, \ldots, u_m)^t$, $f(u,t) =$

$\left(f_1(u,t), f_2(u,t), \ldots, f_m(u,t)\right)^t$ and $c_0 = (c_{0,1}, c_{0,2}, \ldots, c_{0,m})^t$ is the initial condition.

We apply the Waveform-Relaxation method for $i = 1, \ldots m$ and have:

$$\frac{\partial u_{1,i}(x,t)}{\partial t} = f_1\left(u_{1,i}, u_{2,i-1}, \ldots, u_{m,i-1}\right) \text{ with } u_{1,i}(t^n) = u_1(t^n) \tag{25}$$

$$\frac{\partial u_{2,i}(x,t)}{\partial t} = f_2\left(u_{1,i-1}, u_{2,i}, u_{3,i-1}\ldots, u_{m,i-1}\right) \text{ with } u_{2,i}(t^n) = u_2(t^n) \tag{26}$$

$$\vdots$$

$$\frac{\partial u_{m,i}(x,t)}{\partial t} = f_m\left(u_{1,i-1}, u_{2,i-1}, \ldots, u_{m-1,i-1}u_{m,i-1}\right) \text{ with } u_{m,i}(t^n) = u_m(t^n), \tag{27}$$

where we have $u_{1,-1}(t) = u_1(t^n), \ldots, u_{m,-1}(t) = u_m(t^n)$ for the initialisation of the first step.

We reduce to two equations and reformulate the method to our iterative splitting methods. So we deal with:

$$\frac{\partial u_1}{\partial t} = f_{11}(u_1, t) + f_{12}(u_2, t), \text{ in } (0,T), \tag{28}$$

$$\frac{\partial u_2}{\partial t} = f_{21}(u_1, t) + f_{22}(u_2, t), \text{ in } (0,T), \tag{29}$$

$$u(0) = c_0, \tag{30}$$

where $u = (u_1, u_2)^t$.

Our notation for the operator equation is given as:

$$\frac{\partial u}{\partial t} = A(u) + B(u), \text{ in } (0,T), \tag{31}$$

$$u(0) = v_0, \tag{32}$$

where

$$A(u) = \begin{pmatrix} f_{11}(u_1) \\ f_{21}(u_1) \end{pmatrix}, \tag{33}$$

$$B(u) = \begin{pmatrix} f_{12}(u_1) \\ f_{22}(u_1) \end{pmatrix}. \tag{34}$$

The iterative splitting method as Waveform-Relaxation method written for $i = 0, 1, \ldots, m$ is:

$$\frac{\partial u_i}{\partial t} = A(u_{1,i}, u_{2,i-1}) + B(u_{1,i-1}, u_{2,i}) \tag{35}$$

with $u_{1,i}(t^n) = u_1(t^n)$ and $u_{2,i}(t^n) = u_2(t^n)$,

where we have $u_{1,-1}(t) = u_1(t^n)$, $u_{2,-1}(t) = u_2(t^n)$ for the initialisation of the first step.

C. Application of the Waveform-Relaxation method

For an effective application, we modify the Waveform-Relaxation method. We deal with the following equations:

$$\partial_t u_1 = -\lambda_1 u_1 + \lambda_2 u_2 + \ldots + \lambda_m u_m \text{ in } \Omega \times (0,T), \tag{36}$$

$$\vdots$$

$$\partial_t u_m = \lambda_1 u_1 + \lambda_2 u_2 + \ldots - \lambda_m u_m \text{ in } \Omega \times (0,T), \tag{37}$$

$$u(0) = (c_1, \ldots c_m) \in \Omega. \tag{38}$$

The algorithm is given with semi-analytical solutions of the reaction equations

$$\tilde{u}^k = \exp(-\Lambda t)\tilde{u}^0 + \Lambda^{-1}\left(I - \exp(-\Lambda t)\right)\widetilde{\Lambda}\tilde{u}^{k-1}, \tag{39}$$

where the matrices are given as

$$\tilde{u}^k = \begin{pmatrix} u_1^k \\ u_2^k \\ \vdots \\ u_m^k \end{pmatrix}, \tag{40}$$

$$\tilde{u}^{k-1} = \begin{pmatrix} u_1^{k-1} \\ u_2^{k-1} \\ \vdots \\ u_m^{k-1} \end{pmatrix}, \tag{41}$$

$$\Lambda = \begin{pmatrix} \lambda_1 & 0 & \ldots & 0 \\ 0 & \lambda_2 & \ldots & 0 \\ \vdots & \ddots & \ddots & \vdots \\ 0 & 0 & \ldots & \lambda_m \end{pmatrix}, \tag{42}$$

$$\widetilde{\Lambda} = \begin{pmatrix} 0 & \lambda_2 & \ldots & \lambda_m \\ \lambda_1 & 0 & \ldots & \lambda_m \\ \vdots & \ddots & \ddots & \vdots \\ \lambda_1 & \lambda_2 & \ldots & 0 \end{pmatrix}. \tag{43}$$

The iterative algorithm is given as

Step 1: $\tilde{u}^0 = (c_1(x), \ldots, c_m(x))^T$

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Step 2: Solve $\tilde{u}^1$ with

$$\tilde{u}^1 = \exp(-\Lambda t)\tilde{u}^0 + \Lambda^{-1}(I - \exp(-\Lambda t))\widetilde{\Lambda}\tilde{u}^0, \qquad (44)$$

$\vdots$

Step k :

$$\tilde{u}^k = \exp(-\Lambda t)\tilde{u}^0 + \Lambda^{-1}(I - \exp(-\Lambda t))\widetilde{\Lambda}\tilde{u}^{k-1}, \qquad (45)$$

The stop-criterion is controlled after each step:
We have the absolute error of the solution vector
$\left| \tilde{u}^k - \tilde{u}^{k-1} \right| \le \mathrm{err}$

and we finish the algorithm and obtain the results:
$u(t) = u^k(t)$.

Remark 2. For modification to the Waveform-Relaxation method, we have the following contributions:
1.) Gauss-Seidel Waveform-Relaxation Method:
Here we apply the lower matrix for the iteration method.
2.) Block Jacobian Waveform Relaxation Method:
Here we have 2×2 blocks for the diagonals.
3.) Block Gauss-Seidel Waveform Relaxation Method:
Here we have 2×2 blocks for the diagonals and the lower matrix.

V. EXPERIMENT FOR THE PLASMA REACTOR

In the following experiments, we step by step introduce the model-equations for the plasma reactor.

A. Simplified Model
We deal with two species of the reaction system. Based on this small system we apply the numerical and analytical methods to get some experiences.
The decay-factors are given as λ_1 and λ_2.
We have the following equations

$$\partial_t u_1 = -\lambda_1 u_1 + \lambda_2 u_2 \text{ in } \Omega \times (0,T,), \qquad (46)$$

$$\partial_t u_2 = \lambda_1 u_1 - \lambda_2 u_2 \text{ in } \Omega \times (0,T,), \qquad (47)$$

$$u_1(0) = u_{1,0}, \ u_2(0) = u_{2,0} \ \in \Omega, \qquad (48)$$

where the particle densities are given as $u_1 = u_1(t)$ and $u_2 = u_2(t)$ in $(0,T) \subset \mathbb{R}^+$.

The interactions are given with $\lambda_1 = 0.1$ and $\lambda_2 = 0.01$. The initial conditions are given as $u_{1,0} = 1.0$ and $c_{2,0} = 0.1$.

The analytical solutions are given as

$$u_1 = \frac{\lambda_2}{\lambda_1} c_0 + \exp(-(\lambda_1 + \lambda_2)t)(-c_1),$$

$$u_2 = c_0 + \exp(-(\lambda_1 + \lambda_2)t)(c_1),$$

where the values c_0 and c_1 are given as

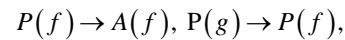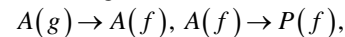$$c_0 = \frac{u_{1,0} + u_{2,0}}{1 + \dfrac{\lambda_2}{\lambda_1}}, \ c_1 = u_{2,0} - c_0$$

The numercial results are given in Fig. 1.

B. Gas adsorption
In a next example we simulate the gas adsorption with a diffusion reaction equation, see [24].

We have reversible reactions of two gas-species which are deposit to a surface (fluid or solid).
We have the following reactions:

$$A(g) \to A(f), \ A(f) \to P(f),$$

$$P(f) \to A(f), \ P(g) \to P(f),$$

where $A(g)$ is reactant A in the gas-phase, $A(f)$ is reactant A in the fluid-phase, $P(g)$ is reactant P in the gas-phase, $P(f)$ is reactant P in the fluid-phase.
We deal with the following reaction rates:

$$R_A = k_1 \left(C_A - \frac{C_P}{K} \right).$$

The thin film can be simulated by:

$$D_{A,f} \frac{\partial^2 C_A}{\partial x^2} = R_A, \qquad (51)$$

$$D_{P,f} \frac{\partial^2 C_P}{\partial x^2} = -R_A, \qquad (52)$$

where C_A is the concentration of reactant A and C_P is the concentration of reactant P.
We have the following boundary conditions:

$$x = 0: \ C_A(x) = C_A^I, \ C_P(x) = C_P^I, \qquad (53)$$

$$x = \delta: \ C_A(x) = \widetilde{C}_A, \ C_P(x) = \widetilde{C}_P. \qquad (54)$$

The analytical solutions are given as:

$$C_A = \frac{\sinh\left(\phi_R\left(1 - \frac{x}{\delta}\right)\right)}{\sinh(\phi_R)} \frac{KC_A^I - C_P^I}{K + \upsilon} + \frac{\sinh\left(\phi_R \frac{x}{\delta}\right)}{\sinh(\phi_R)} \frac{K\widetilde{C}_A - \widetilde{C}_P}{K + \upsilon} + \left(1 - \frac{x}{\delta}\right)\frac{\upsilon C_A^I - C_P^I}{K + \upsilon} + \frac{x}{\delta}\frac{\upsilon\widetilde{C}_A - \widetilde{C}_P}{K + \upsilon}, \qquad (55)$$

and

$$C_P = C_P^I + \upsilon(C_A^I - C_A) - \frac{x}{\delta}\left(\upsilon(C_A^I - \widetilde{C}_A) + (C_P^I - \widetilde{C}_P)\right) \quad (56)$$

In the Fig. 2, we have simulated the gas-sorption with the following parameters:
$k_1 = 0.01, \ K = 1.0, \ \delta = 1.0$
$C_A^I = 1.0, \ C_P^I = 0.5$
$\widetilde{C}_A = 1.0, \ \widetilde{C}_P = 0.5$
$D_{A,f} = 0.01, \ D_{P,f} = 0.02,$

where $\phi_R = \delta\sqrt{\dfrac{k_1(K+\upsilon)}{D_{A,f}K}}$ and $\upsilon = \dfrac{D_{A,f}}{D_{P,f}}$.

In the result, we obtain a balance of the reactant A which is most decaying in the middle of the time-period, the relaxation takes place in the second period and at least some concentation is obtained. Here the deposition has only a very small time-period in which the second reactant P can influence the process.

C. Test-examples with three Species solved with analytical methods
In the following experiment we deal with the analytical method to get the numerical solution of a coupled differential

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equation system with three equations. We have taken into account 1000 time steps. The analytical method is based on a transformation to an eigenvalue problem and this method can be used to solve the results with the Waveform-Relaxation method.

The reaction is given as
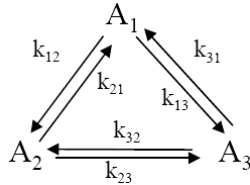
The equation is given as, cf. [16]:

$$\partial_t a_1 = -(k_{12} + k_{13})a_1 + k_{21}a_2 + k_{31}a_3 \text{ in } \Omega \in (0,T), \quad (57)$$

$$\partial_t a_2 = k_{12}a_1 - (k_{21} + k_{23})a_2 + k_{32}a_3 \text{ in } \Omega \in (0,T), \quad (58)$$

$$\partial_t a_3 = k_{13}a_1 + k_{23}a_2 - (k_{31} + k_{32})a_3 \text{ in } \Omega \in (0,T), \quad (59)$$

$$a_0 = (c_1, c_2, c_3) \quad (60)$$

We solve the equation with analytical methods, cf. [16] with three species.

We have the following parameters:

$$c_1 = c_2 = c_3 = \frac{1}{3},$$

$$k_{12} = 0.50, \ k_{21} = 0.25, \ k_{13} = 0.20,$$

$$k_{31} = 0.05, \ k_{23} = 0.30, \ k_{32} = 0.15$$

The end-time is given as $T = 10.0$.

In Fig. 3 we have simulated the three species. The end concentration of the species results in a loss of concentration of A_1 (first species), a nearly balance of concentration of A_2 (second species) and a tremendous increase of concentration of A_3 (third species). So at least the reaction on this end situation has taken place from A_1 to A_3.

D. Real-life example: Sputtering Reactions

In the following experiment, we deal with the sputtering reactions which is discussed in [4].

The CVD-process has different chemical reactants, which react and decay in different time periods. We concentrate on a simple sputtering reaction, which has at least seven reactants.

The reactions is given as
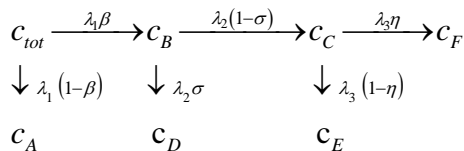
We have the following reaction equations:

$$\partial_t c_{tot} = -\lambda_1 c_{tot}, \quad (61)$$

$$\partial_t c_A = \lambda_1 (1-\beta) c_{tot}, \quad (62)$$

$$\partial_t c_B = \lambda_1 \beta c_{tot} - \lambda_2 c_B, \quad (63)$$

$$\partial_t c_C = \lambda_2 (1-\sigma) c_B - \lambda_3 c_C, \quad (64)$$

$$\partial_t c_D = \lambda_2 \sigma c_B, \quad (65)$$

$$\partial_t c_E = \lambda_3 (1-\eta) c_C, \quad (66)$$

$$\partial_t c_F = \lambda_3 \eta c_C, \quad (67)$$

where c_{tot} is the total mass of the particles coming from the substrate. c_A, c_B, c_C, c_D, c_E and c_F are intermediate masses of the particles, only c_A and c_F arrive at the targets.

We have the following reaction-matrix :

$$A = \begin{pmatrix} -\lambda_1 & 0 & 0 & 0 & 0 & 0 & 0 \\ \lambda_1(1-\beta) & 0 & 0 & 0 & 0 & 0 & 0 \\ \lambda_1\beta & 0 & -\lambda_2 & 0 & 0 & 0 & 0 \\ 0 & 0 & \lambda_2(1-\sigma) & -\lambda_3 & 0 & 0 & 0 \\ 0 & 0 & \lambda_2\sigma & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \lambda_3(1-\eta) & 0 & 0 & 0 \\ 0 & 0 & 0 & \lambda_3\eta & 0 & 0 & 0 \end{pmatrix}. \quad (68)$$

We apply an analytical method, cf. [16].
We have the following parameters:

$$c_{A,0} = \ldots = c_{F,0} = 0.1,$$

$$c_{tot,0} = 1.0,$$

$$\lambda_1 = \lambda_2 = 0.1, \ \lambda_3 = 0.05,$$

$$\beta = 0.1, \ \sigma = 0.5 \ \eta = 0.9$$

The end-time is given as $T = 10.0$.

In Fig. 4 we have simulated the sputtering reactions. In the results, we obtain the arrival of the c_A and c_F mass particles. The first deposition of c_{tot} results in c_A. The second deposition of c_{tot} results, due to the reaction chain, in c_F and is tremendous decreasing. In our final time situation we have approximately 0.8 amount of the initial concentration that rests on the targets. As a result we loose nearly 20 % of the substrate and should additionally increase our source substrate to 1.2 amounts.

VI. CONCLUSIONS AND DISCUSSIONS

We present a plasma model for thin layers. The models are given as diffusion-reaction equations. The efficient Waveform-Relaxation method is used for the chemical reaction equations. We discuss various applications og chemical reactions. The results verify the theoretical investigations and we simulate a real life apparatus with sputtering reactions.

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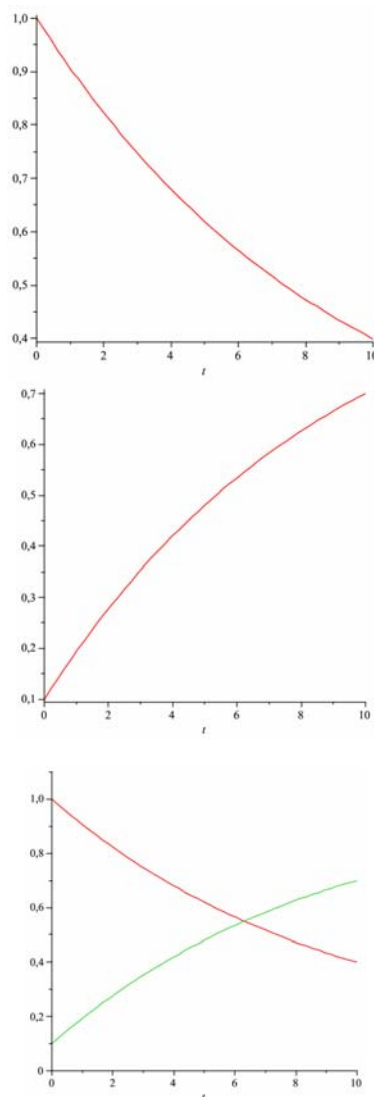
Fig.1 Experiment of a two species reaction, $\lambda_1 = 0.1$, $\lambda_2 = 0.01$, upper figure: c_1, middle figure: c_2, lower figure: c_1 (red), c_2 (green).

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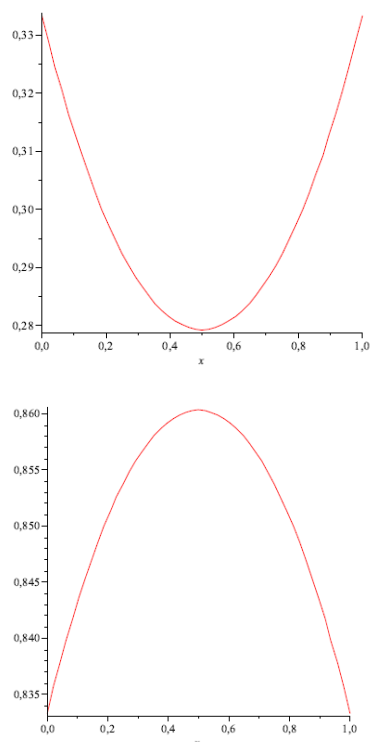International Journal of Chemical and Molecular Engineering
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Fig. 2 Experiment with the gas-sorption of two species, upper figure: C_A, lower figure: C_P.
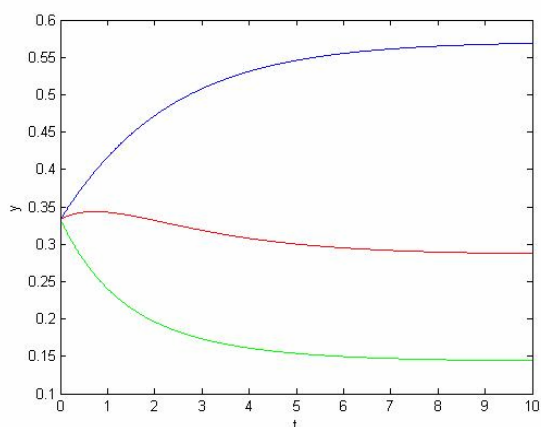

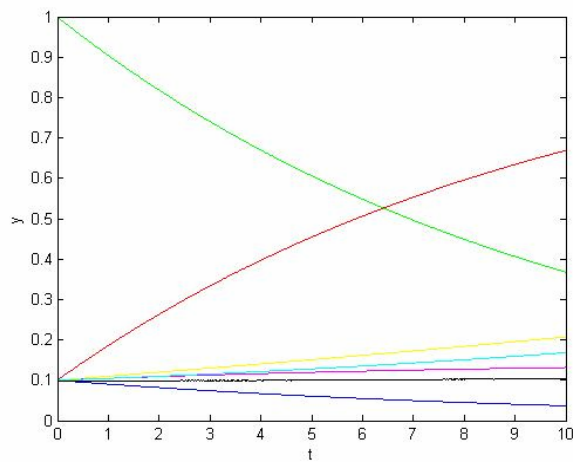Fig. 3 Experiment of a three species reaction: a_1 (green), a_2 (red), a_3 (blue)
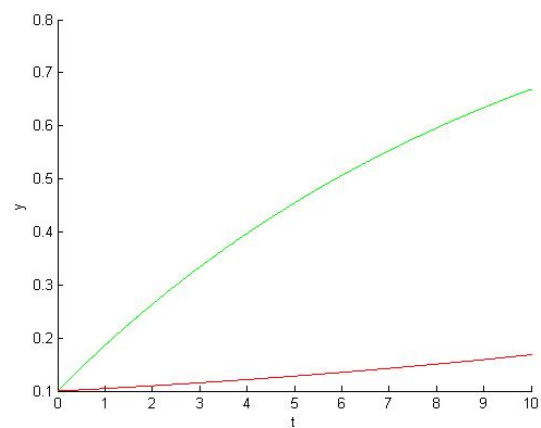

Fig. 4 Experiment of a seven species reaction: upper figure: c_A (green), c_F (red); lower figure: c_{tot} (green), c_A (red), c_B (blue), c_C (yellow), c_D (magenta), c_E (black), c_F (cyan)