

# Comparison of numerical methods for transient CVD simulations

S. Van Veldhuizen<sup>a,\*</sup>, C. Vuik<sup>a</sup>, C.R. Kleijn<sup>b</sup>

<sup>a</sup> Delft University of Technology, Delft Institute of Applied Mathematics, Mekelweg, 4, 2628 CD Delft, The Netherlands

<sup>b</sup> Delft University of Technology, Department of Multi Scale Physics, Prins, Bernardlaan 6, 2628 BW Delft, The Netherlands

Available online 18 April 2007

## Abstract

The numerical modeling of laminar reacting gas flows in thermal Chemical Vapor Deposition (CVD) processes commonly involves the solution of convection–diffusion–reaction equations for a large number of reactants and intermediate species. These equations are stiffly coupled through the reaction terms, which typically include dozens of finite rate elementary reaction steps with largely varying rate constants. The solution of such stiff sets of equations is difficult, especially when time-accurate transient solutions are required. The latter is important for the study of start-up and shut-down cycli, but also for the study of inherently transient CVD processes, such as Rapid Thermal CVD (RTCVD) and Atomic Layer Deposition (ALD). In this study various numerical schemes for multidimensional transient simulations of laminar reacting gas flows with homogeneous and heterogeneous chemical reactions are compared in terms of efficiency, accuracy and robustness. As a test case, we study the CVD process of silicon from silane, modeled according to the classical 16 species, 27 reactions chemistry model for this process as published by Coltrin and coworkers [M.E. Coltrin, R.J. Kee, G.H. Evans, J. Electrochem. Soc. 136 (1989) 819]. We validate our results by comparison to steady state solutions in the benchmark paper of Kleijn [C.R. Kleijn, Thin Solid Films, 365 (2000) 294]. It is concluded that, for time-accurate transient simulations of the stiff chemistry problems in CVD modeling the conservation of the non-negativity of the species concentrations is much more important, and much more restrictive towards the time step size, than stability. For the time integration methods studied in this paper, we give suggestions for the associated optimal nonlinear and linear solvers, such that the total computational costs are reduced as much as possible.

© 2007 Elsevier B.V. All rights reserved.

*Keywords:* Chemical Vapor Deposition; Numerical Simulations; Modeling; Numerical Stiffness; Time Integration; Positivity

## 1. Introduction

The growth of thin solid films via Chemical Vapor Deposition (CVD) is of considerable importance in the micro-electronics industry. Other applications of thin solid films via CVD can for instance be found in the glass industry as protective and decorative layers. The CVD process considered in this paper involves the deposition of silicon in an atmospheric pressure, cold wall, stagnation flow single wafer reactor, starting from the thermal decomposition of silane at the heated susceptor surface. This CVD process was one of the very first for which a detailed chemistry model, based on a large number of elementary reaction steps leading to the formation of many intermediate species, has been proposed in literature [1]. The numerical modeling of realistic CVD processes and equipment, based on such detailed

chemistry models, involves the solution of multi-dimensional convection–diffusion–reaction equations for a large number of reactants and intermediate species. These equations are stiffly coupled through the reaction terms, which typically include dozens of finite rate elementary reaction steps with largely varying rate constants. The solution of such stiff sets of equations is difficult, and the numerical solvers present in most commercial CFD codes have great problems in handling such stiff systems of equations. This is especially the case when time-accurate transient solutions are required. The latter is important for the study of start-up and shut-down cycli, but also for the study of inherently transient CVD processes, such as RTCVD and ALD.

In this paper we focus on solving the system of species equations, which describe mass transport due to convective and diffusive transport, and their conversion due to chemical reactions, in a time accurate way. Since there may be orders of magnitude difference between the time scales of advection, diffusion and the various chemical reactions, the system of species equations is extremely stiff. To stably integrate the species equations in time, a suitable time integration method has

\* Corresponding author. Tel.: +31 15 278 7608; fax: +31 15 278 7209.

E-mail address: [s.vanveldhuizen@tudelft.nl](mailto:s.vanveldhuizen@tudelft.nl) (S. Van Veldhuizen).

<sup>1</sup> This author's work was supported by the Delft Centre for Computational Science and Engineering.

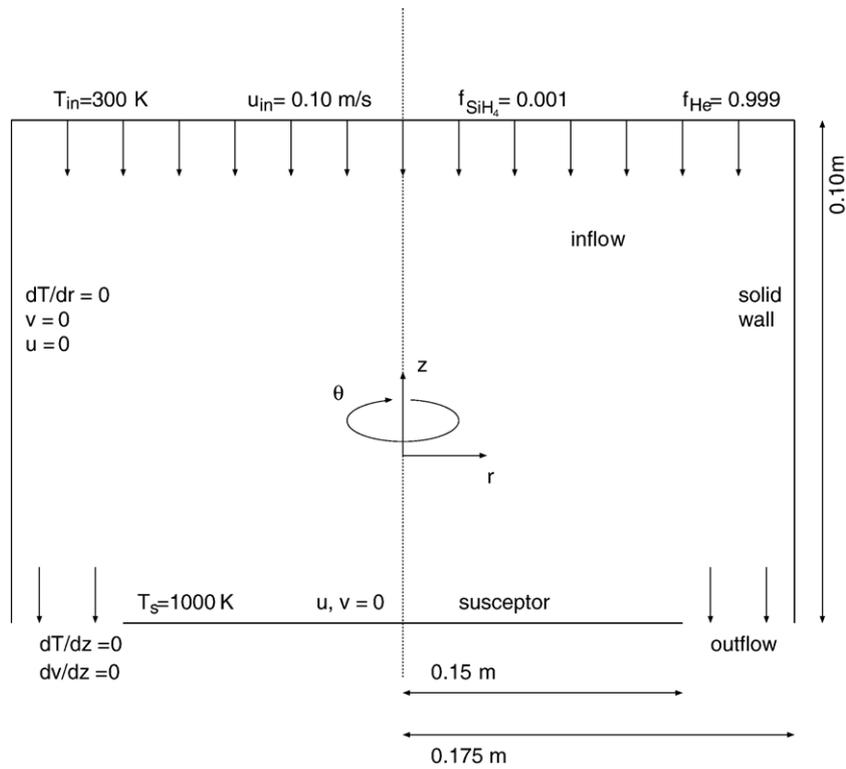


Fig. 1. Reactor geometry and boundary conditions.

to be found. Moreover, we demand that negative species concentrations are not allowed in the transient solution, because they cause blow up of the solution in finite time, see, for instance, [3]. Since we do not want to apply clipping, and thus artificially add mass to the system, this extra property puts a severe restriction on time integration methods.

This paper is organized as follows. First we give details of the CVD process considered in this paper, followed by a brief overview of the numerical methods that we used to do the experiments. We conclude with some transient numerical results.

## 2. Model equations

The model assumptions and equations used have been described in great detail in [4]. The gas mixture is assumed to behave as a continuum, Newtonian fluid. The composition of the  $N$  component gas mixture is described in terms of mass fractions  $\omega_i$ ,  $i = 1, \dots, N$ . In this paper we focus on the time accurate numerical solution of the nonlinearly, stiffly coupled set of species equations,  $i = 1, \dots, N$ ,

$$\frac{\partial(\rho\omega_i)}{\partial t} = -\nabla \cdot (\rho\mathbf{v}\omega_i) + \nabla \cdot [(\rho\mathbb{D}'_i \nabla \omega_i) + (\mathbb{D}'_i \nabla(\ln T))] + m_i \sum_{k=1}^K v_{ik} R_k^g, \quad (1)$$

where the diffusive mass flux is composed of concentration and thermal diffusion.

The studied reactor is illustrated in Fig. 1, where as computational domain one half of the  $(r-z)$  plane is taken. From the top a gas-mixture, consisting of 0.1 mole% silane diluted in

helium, enters the reactor with a uniform temperature  $T_{in} = 300$  K and velocity  $\mu_{in} = 0.1$  m/s. In the hot region above the susceptor with temperature  $T_s = 1000$  K the reactive gas silane decomposes into silylene and hydrogen. In the model of Coltrin and coworkers [1], which was used in this paper, this first gas phase reaction initiates a chain of 25 homogeneous gas phase reactions leading to the (de)formation of 14 silicon containing gas phase species. Each of these silicon containing species may diffuse towards the susceptor to produce a thin solid film.

There is some ambiguity as to which values were used in [1], in the present work we followed the approach used in [4], i.e., we set the sticking coefficient of  $\text{Si}_2\text{H}_5$  equal to one, the sticking coefficient of  $\text{Si}_3\text{H}_8$  equal to zero and for the other species the values as were used in [1].

## 3. Numerical methods

The species equations are first discretized in space, and thereafter integrated in time. For spatial discretization a hybrid Finite Volume (FV) scheme has been used, which uses central differences if possible and first order upwinding if necessary. More information on the hybrid FV scheme can be found in, for instance, [5]. It should be noted that the hybrid FV discretization conserves the non-negativity of the solution.

Implicit treatment of the reaction terms, when integrating in time, is needed for stability reasons. When, in addition, also the positivity of the solution is needed, this results in an extra, severe condition on the time step size.

Moreover, it has been proven in [3], that the first order accurate Euler Backward time integration method is the only known method being unconditionally positive (and stable). Every higher

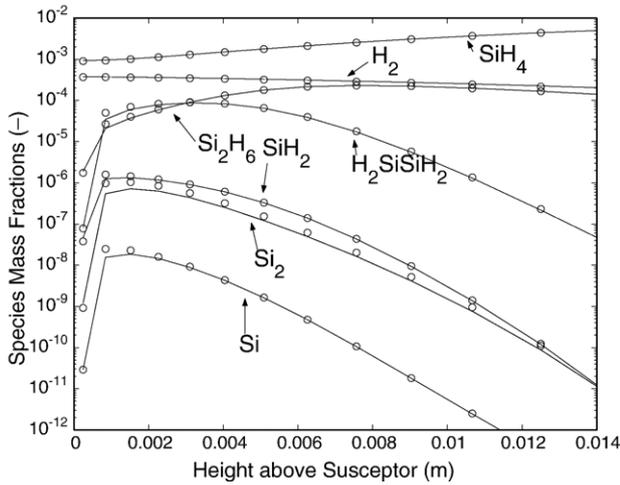


Fig. 2. Axial steady state concentration profiles along the symmetry axis for some selected species. Solid lines are Kleijn's solutions [4], circles are long time steady state results obtained with the present transient time integration methods.

order time integration method will need impractically small time steps to integrate the solution positively. However, in this paper we test next to EB, also the second order accurate Rosenbrock scheme ROS2, the second order BDF2 scheme, and the second order IRKC scheme. To test these schemes seems to contradict with the previous remark, but each of these higher order methods have their advantages. As has been experienced in several tests, see [3], the ROS2 scheme performs well with respect to positivity. For the BDF2 scheme the positivity condition can be computed explicitly, and the IRKC scheme is designed to integrate convection–diffusion–reaction schemes very efficiently. More information on these time integration schemes can be found in [3,7]. For the recently developed IRKC scheme, which integrates the moderately stiff convection–diffusion part of the species equations explicitly, and the reaction part implicitly, we refer to [8]. Since a validated software version of [8] is not available, we adjusted the IRKC solver for stiff diffusion–reaction PDEs

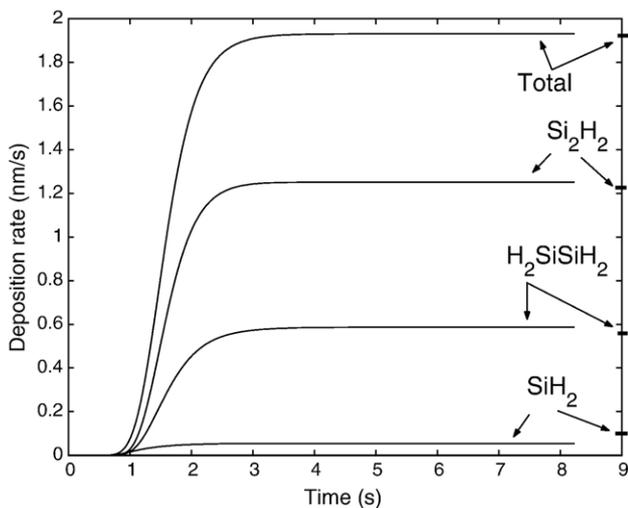


Fig. 3. Transient deposition rates due to some selected species on the symmetry axis for simulations with a non-rotating wafer at 1000 K. On the right vertical axis: steady state deposition rates obtained with Kleijn's steady state code [4].

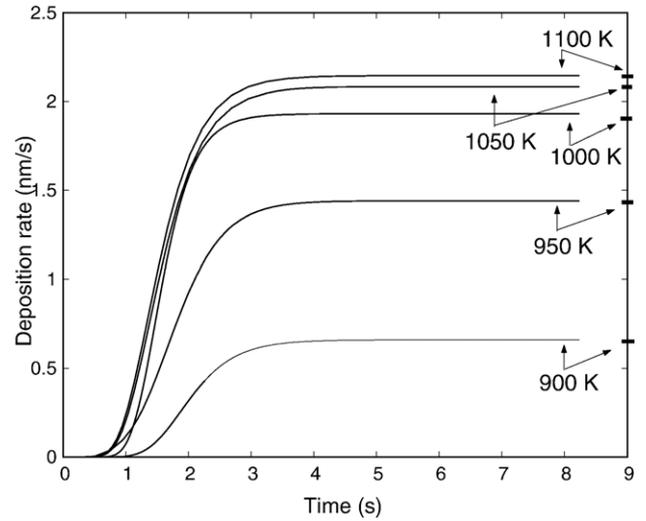


Fig. 4. Transient total deposition rates on the symmetry axis for wafer temperatures varying from 900 K up to 1100 K. On the right vertical axis: steady state total deposition rates obtained with Kleijn's steady state code [4].

available through [8], such that it is available for the integration of stiff convection–diffusion–reaction equations. These adjustments of the IRKC code of [6] are described in [8].

The nonlinear systems arising from the implicit treatment of the species equations are solved by means of a Newton solver, which, if necessary, uses global convergence techniques like linesearch [7]. For a comprehensive description of the (non) linear solvers used, we refer to [7].

#### 4. Results

Since the reactants are highly diluted in the carrier gas helium, we use the steady state velocity fields, temperature field, pressure field and density field computed by Kleijn [4]. For such systems, the computation of the laminar flow and temperature

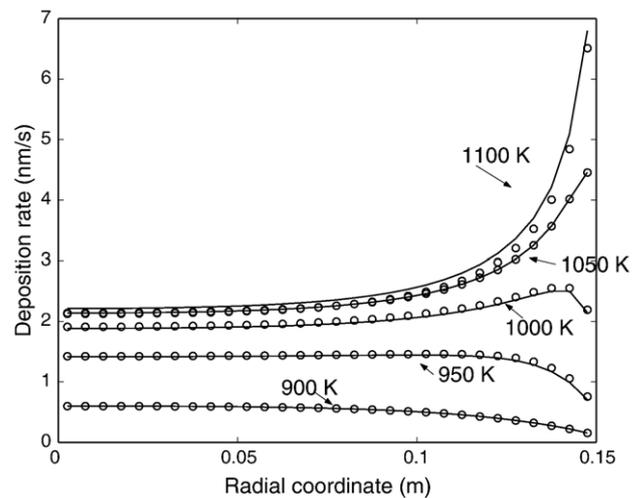


Fig. 5. Radial profiles of the total steady state deposition rate for wafer temperatures varied from 900 K up to 1100 K. Solid lines are Kleijn's steady state results, circles are long time steady state results obtained with the present transient time integration method.

Table 1  
Integration statistics for EB, BDF2, ROS2 and IRKC, with full Newton solver

Number of	EB	BDF2	ROS2	IRKC
$F$	190	757	424	42,7911
$F'$	94	417	142	2008
Linesearch	11	0	0	30
Newton iters	94	417	0	17,331
Rejected time steps	1	10	2	728
Accepted time steps	38	138	140	1284
CPU Time	6500	30,500	8000	19,500

fields etc., is, in comparison with computation of the species mass fractions, a relatively trivial task. The simulations start from the instant that the reactor is completely filled with the carrier gas helium and a mixture of helium and silane starts to enter the reactor, and stop when steady state is obtained. Correctness of our solution is then validated against the steady state solution obtained with the software of Kleijn [4]. All simulations presented in this paper are test cases where the wafer is not rotating.

In Fig. 2 steady state mass fraction profiles are presented for some selected species, as well as the ones obtained by Kleijn [4], for a wafer temperature equal to 1000 K. In this case, the total steady state deposition rate of silicon at the symmetry axis as found by Kleijn [4] is 1.92 nm/s, whereas we found a deposition rate of 1.93 nm/s. Both values compare excellently to those obtained with the well-known 1-dimensional CVD simulation code SPIN within the Chemkin family [2]. In Fig. 3 transient deposition rates are presented for some selected species, as well as the transient total deposition rate. It can be seen that the time dependent behavior of these deposition rates is monotonically increasing and stabilizes when the solution is in steady state.

In Fig. 4 we present transient total deposition rates for simulations with wafer temperatures varying from 900 K up to 1100 K. The time dependent behavior of all deposition rates is monotonically increasing until the species concentrations are in steady state. Note that the relative contributions of the various silicon containing species to the total deposition rate is a function of the wafer temperatures, with the relative contribution of  $\text{Si}_2\text{H}_2$  increasing with increasing temperature, and the relative contribution of  $\text{H}_2\text{SiSiH}_2$  decreasing with increasing temperature. Fig. 5 shows radial profiles of the total steady state deposition rates of both Kleijn's steady state computations [4], and our steady state results obtained with the time integration methods as discussed in Section 3, for wafer temperatures varied from 900 K up to 1100 K. Again, the agreement is for all wafer temperatures excellent. For all studied temperatures, the steady state growth rates obtained with the present transient solution method were found to differ less than 5% from those obtained with Kleijn's steady state code.

The integration statistics of the various time integration methods mentioned in Section 3 are presented in Table 1. Based

upon these experiments we conclude that the unconditionally stable and positive time integration method Euler Backward is the cheapest in terms of computational costs. However, the second order ROS2 scheme performs also quite well, although it is not unconditionally positive for the species equations, see [7]. When the convection part is omitted, then the ROS2 scheme becomes unconditionally positive. This property explains probably the good behavior with respect to positivity for the convection–diffusion–reaction case. The performance of the IRKC scheme is between BDF2 and ROS2. The relative large number of rejected time steps in IRKC is mainly due to a failure with respect to positivity. Due to its special structure, the direct solvers within the IRKC scheme are also applicable in 3D simulations, whereas the other schemes have to switch to iterative linear solvers.

## 5. Conclusions and future research

In terms of computational costs the Euler Backward scheme is the best choice. In spite of its conditional positivity, the ROS2 scheme performed quite well in comparison with the other higher order integration methods. However, for time accurate simulations on 3D geometries, we expect that the IRKC scheme will perform better, because the convection–diffusion terms are solved explicitly. The only systems to be solved originate from the reaction terms, and the corresponding dimension remains the same when going from 2 to 3 spatial dimensions; this dimension equals the number of species. The other time integration methods have to switch to iterative linear solvers, where appropriate preconditioners have to be developed. For problems from chemistry, like the one in this paper, this is still a challenging task for future research.

## References

- [1] M.E. Coltrin, R.J. Kee, G.H. Evans, *J. Electrochem. Soc.* 136 (1989) 819.
- [2] M.E. Coltrin, R.J. Kee, G.H. Evans, E. Meeks, F.M. Rupley, J.F. Grear, SPIN (version 3.83): a FORTRAN program for modeling one-dimensional rotatingdisk/stagnation-flow chemical vapour deposition reactors, Technical Report SAND91-8003.UC-401, Sandia National Laboratories, Albuquerque, 1993.
- [3] W. Hundsdorfer, J.G. Verwer, *Numerical solution of time-dependent advection–diffusion–reaction equations*, Springer Series in Computational Mathematics, vol. 33, Springer, Berlin, 2003.
- [4] C.R. Kleijn, *Thin Solid Films* 365 (2000) 294.
- [5] S.V. Patankar, *Numerical Heat Transfer and Fluid Flow*, Hemisphere Publishing Corp., Washington DC, 1980.
- [6] L.F. Shampine, B.P. Sommeijer, J.G. Verwer, *J. Comput. Appl. Math.* 196 (2006) 485.
- [7] S. Van Veldhuizen, C. Vuik, C.R. Kleijn, Comparison of ODE Methods for Laminar Reacting Gas Flow Simulations, *Num. Meth. Part. Diff. Eq.*, (submitted for publication).
- [8] J.G. Verwer, B.P. Sommeijer, W. Hundsdorfer, *J. Comp. Phys.* 201 (2004) 61.