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A LABORATORY REACTOR FOR KINETIC STUDIES OF GAS-SOLID REACTIONS AT LOW PRESSURES: DESIGN AND MODELLING IN THE PRESENCE OF IRREDUCIBLE TRANSPORT PHENOMENA

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Abstract - A continuous flow laboratory reactor designed for kinetic studies of gas-solid reactions at low pressures is described. Its application is illustrated by the low pressure chemical vapour deposition (LPCVD) of polycrystalline silicon. Mixing in the reactor is based on molecular diffusion. On-line monitoring of the deposition rate is performed with a microbalance. A mathematical model to analyse the experimental data is presented. Special attention is paid to the effects of irreducible concentration gradients of gas phase intermediates. By taking these effects quantitatively into account it is possible to obtain rate coefficients which are intrinsic, i.e. only determined by chemical phenomena.

INTRODUCTION

Even under isothermal conditions gas-solid reactions, such as coking and chemical vapour deposition (CVD), will not lead to uniform deposition in tubular reactors. To develop reaction schemes for such reactions, information about local deposition rates combined with the corresponding gas phase composition is needed, see e.g. Sundaram and Froment (1974).

To investigate the intrinsic kinetics of the low pressure CVD of polycrystalline silicon, a laboratory reactor setup has been designed which satisfies both of the above prerequisites during continuous flow experiments. The investigated conditions are similar to those of conventional hot-wall multiwafer LPCVD reactors, i.e. 10-100 Pa total pressure and temperatures from 850-950 K. Because of the low pressures employed the reactor configuration cannot provide for plug flow conditions as mass Peclet numbers are typically in the range 0.1-10. Owing to fast molecular diffusion, starting from ideal mixing therefore was considered more promising.

The present contribution addresses the design of the laboratory reactor and the mathematical modelling of experimental data obtained with it. It is shown that when there is a significant contribution to the deposition rate of polycrystalline silicon by intermediates formed in the gas phase, the concentration gradients of the latter cannot be neglected. The corresponding so-called irreducible transport limitations have to be accounted for in order to obtain intrinsic kinetic information from the experiments.

POLYCRYSTALLINE SILICON DEPOSITION

Silicon deposition is known to occur according to a complex reaction mechanism, see e.g. Coltrin *et al.* (1986). A large number of reactive intermediates is formed in the gas phase exhibiting very high reaction probabilities with the deposition surface thereby leading to solid silicon.

A set of elementary reactions, the most important of which are listed in Table 1, was shown to describe adequately the growth of polycrystalline silicon from silane over a wide range of conditions (Weerts, 1995). Reactions (1) to (4) describe the gas phase kinetics. The adsorption of the silicon hydride components, e.g. reactions (5) to (7), is followed by a further dehydrogenation of the surface species to solid silicon and an associative desorption of hydrogen, reaction (8).

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Table 1 Some important reactions and corresponding rate coefficients at 100 Pa and 900 K, 100% SiH₄ during polycrystalline silicon deposition in the gas phase (1-4) and on the silicon surface (5-8) (Weerts, 1995)

Gas phase	k/s^{-1} or $m^3 mol^{-1} s^{-1}$	Surface
(1) $SiH_4 \rightleftharpoons SiH_2 + H_2$	$1.05 \cdot 10^{-2}$	(5) $SiH_4 + 2^* \rightarrow SiH_3^* + H^*$
(2) $SiH_4 + SiH_2 \rightleftharpoons Si_2H_6$	$3.46 \cdot 10^6$	(6) $SiH_2 + ^* \rightarrow SiH_2^*$
(3) $Si_2H_6 \rightleftharpoons H_3SiSiH + H_2$	$1.00 \cdot 10^1$	(7) $Si_2H_6 + ^* \rightarrow SiH_4 + SiH_2^*$
(4) $H_3SiSiH \rightleftharpoons H_2 SiSiH_2$	$3.43 \cdot 10^6$	(8) $2H^* \rightleftharpoons H_2 + 2^*$

REACTOR DESIGN

The laboratory reactor setup consists of a quartz continuous flow reactor. Spherical geometry was chosen because it favours mixing and uniformity of heat transfer. After premixing, the feed mixture is preheated to overcome intrareactor temperature gradients and injected through the four nozzles of a cross-shaped injector, located in the middle of the reactor. The nozzles with inner diameter $9.0 \cdot 10^{-4}$ m are located midway between the centre of the reactor and the wall, in two orthogonal planes. The inner diameter of the reactor is $6.0 \cdot 10^{-2}$ m and the inner diameter of the reactor outlet is $2.2 \cdot 10^{-2}$ m. The above reactor configuration, see figure 1, permits mean residence times between 0.1 and 1 s at typical LPCVD conditions. In the middle of the reactor, just above the cross-shaped injector, a 10×15 mm² sized silicon sample is suspended from a microbalance. Prior to each series of experiments the silicon sample and reactor wall are pre-coated with polycrystalline silicon at 50 Pa and 900 K during 30 minutes, after pretreatment with hydrogen at 900 K during 10 minutes. On-line analysis of the gas mixture is performed with a differentially pumped quadrupole mass spectrometer (QMS), connected via an all-metal orifice inlet to the outlet of the reactor. For quantitative analysis the QMS is calibrated for silane and disilane prior to each series of experiments.

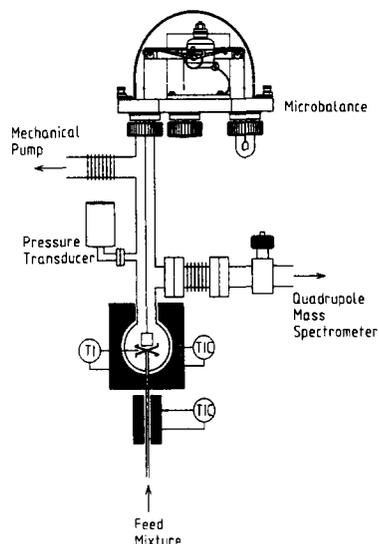


Figure 1: Laboratory reactor for kinetic studies of polycrystalline silicon deposition.

MIXING PERFORMANCE

At the low pressures employed molecular diffusion coefficients are roughly three orders of magnitude larger than at atmospheric pressure and molecular diffusion will thus be the most important mode of mass transport in the reactor. Using realistic values for molecular diffusion coefficients in binary SiH₄/H₂ mixtures it can be calculated that concentration uniformity within 1% of the mean is achieved after $1 \cdot 10^{-3}$ s at 100 Pa and 900 K, implying that reactor scale mixing by molecular diffusion is fast compared to the mean residence time. This was verified by spatial concentration measurements of a tracer gas continuously fed through an inlet close to the nozzles. Concentration uniformity within 5% of the mean is

achieved at residence times of 0.1 s. Of course, classical residence time distribution measurements were also performed in order to assess the degree of macromixing. In this case, however, the observed residence time distribution was almost completely determined by the transport in the inlet tube where a relatively high pressure exists.

Micromixing effects become important in case of non-(pseudo)-first order reactions with reaction times comparable to or smaller than the micromixing time. To estimate the effects of micromixing, calculations of the gas phase composition during silicon LPCVD assuming either complete segregation or ideal micromixing were performed, using the subset of gas phase reactions in Table 1. It was concluded that first and pseudo-first order reactions dominate the gas phase chemistry in view of the agreement between both calculated compositions. As silane and hydrogen are present in large amounts and exhibit spatial uniformity, all considered gas phase reactions are indeed first order or pseudo-first order and thus insensitive to the degree of micromixing.

Spatial temperature uniformity was verified experimentally through thermocouple measurements at fixed positions inside the reactor. These measurements showed that in the temperature range considered, i.e. 800-1000 K, radial temperature gradients can be neglected. The maximum spherically averaged temperature difference between reactor centre and reactor wall occurs at 1000 K and amounts to 3 K.

IRREDUCIBLE TRANSPORT LIMITATIONS

Due to the high surface reaction probability of the gas phase intermediates formed during the pyrolysis of silane, it is necessary to account for the mass transfer resistances of these species during the simulation of the kinetic experiments performed in the reactor setup. The shape of the concentration profiles can be shown to be a complex function of the Damköhler-II number based on the surface kinetics, and a modified Thiele modulus, based on the gas phase kinetics (Weerts, 1995). Depending on the values of these numbers, the concentration gradients of the gas phase intermediates are located within a few millimeter from the growing silicon layer or throughout the complete reactor: the lower the Da_{II} number and the higher the Thiele modulus, the larger the fraction of the gas phase reaction volume with a uniform concentration. Figure 2 shows a typical silylene (SiH_2) concentration profile when only deposition on the reactor wall is considered. The substantial decrease of the concentration near the wall is caused by the high reaction probability with the growing layer as evidenced by the high Da_{II} number. Disilane (Si_2H_6) has a similar reaction probability with solid silicon but a much lower gas phase reactivity leading to a concentration gradient stretching out over the entire gas phase. Disilene (H_2SiSiH_2) and silylsilylene (H_3SiSiH) possess higher gas phase and similar surface reactivities resulting in uniform concentrations throughout the major part of the reactor with a concentration gradient localized near the reactor wall.

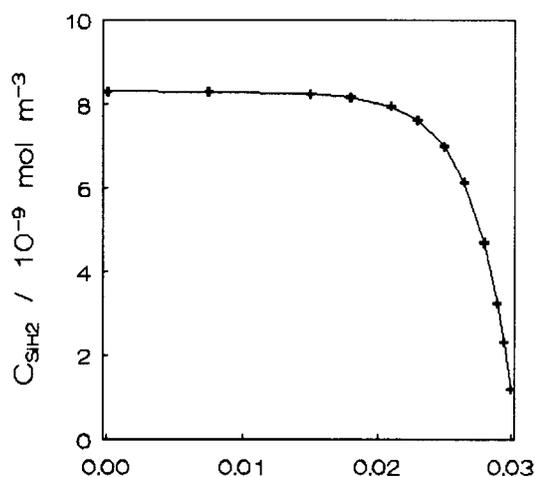


Figure 2: Calculated silylene concentration versus radial reactor coordinate. Conditions: $p_1 = 100 \text{ Pa}$, $T = 900 \text{ K}$, $F_v = 2.26 \cdot 10^{-4} \text{ m}^3 \text{ s}^{-1}$, $C_{SiH_2}^{SSA} = 8.3 \cdot 10^{-9} \text{ mol m}^{-3}$, $Da_{II} = 60.4$, $\phi = 11.2$.

MODEL EQUATIONS

Since molecular diffusion is the only mode of mass transport in the reactor, the Navier-Stokes equations do not have to be considered. Also, there is no need to integrate the enthalpy balance, because of the measured spatial temperature uniformity in the reactor. Consequently, the gas phase model equations reduce to the continuity equations for the gas phase components. The mass transfer between gas phase and deposition surface is accounted for by considering molecular diffusion with simultaneous gas phase reactions. The reaction volume consists of a spherical shell of thickness $R_1 - R_0$. Deposition is considered to

occur on the surfaces at $r = R_0$ and $r = R_1$ enclosing this shell. The radial positions R_0 ($1.396 \cdot 10^{-2}$ m) and R_1 ($3.097 \cdot 10^{-2}$ m) were derived from the values of the total deposition surface area, i.e. $A_d = 1.45 \cdot 10^{-2}$ m², and gas phase reaction volume, i.e. $V_g = 1.13 \cdot 10^{-4}$ m³, during a typical kinetic experiment. The inlet and outlet molar flow rates of each component are treated as source terms in the corresponding continuity equations. For reactive feeds both gas phase consumption and surface consumption need to proceed slowly compared to the mixing process on reactor scale to reach uniform concentrations before leaving the reactor. As this is the case a fast concentration uniformization makes the location of the inlet arbitrary. The outlet molar flow rates are also spread out over the reaction volume and coupled to the molar fractions locally existing. In this way it is explicitly assumed that a fluid element has no measurable interaction with other fluid elements on its way to the reactor outlet. This of course is an ideal situation. Mass interchange is important in the laboratory reactor. The error introduced by the assumption that non-interacting fluid elements are leaving the reactor is dependent on the shape of the concentration profiles, *vide supra*. Errors will be absent in case of flat concentration profiles.

The continuity equation for gas phase component i becomes:

$$\frac{1}{r^2} \frac{d}{dr} (r^2 N_i) = \sum_{k=1}^{ng} v_{k,i} r_{v,k} + (F_{i,o} - y_i F) / V_g \quad (1)$$

The Stefan-Maxwell equations are applied:

$$\frac{dy_i}{dr} = \sum_{j \neq i} \frac{y_i N_j - y_j N_i}{CD_{ij}} \quad (2)$$

with the binary diffusion coefficients calculated using the Chapman-Enskog relations (Reid *et al.*, 1987). Deposition is accounted for through the boundary conditions at $r = R_1$ and $r = R_0$:

$$r = R_0 \quad N_i = \sum_{m=1}^{ns} v_{m,i} r_{a,m} \quad (3)$$

$$r = R_1 \quad N_i = - \sum_{m=1}^{ns} v_{m,i} r_{a,m} \quad (4)$$

In this way (NG-1) molar fractions and NG molar fluxes are defined. The molar fraction of the NG th species follows from:

$$\sum_{i=1}^{NG} y_i = 1 \quad (5)$$

At steady state, the continuity equation for surface component l is given by:

$$\sum_{m=1}^{ns} v_{m,l} r_{a,m} = 0 \quad (6)$$

In this way (NS-1) surface concentrations are defined. The NS th surface concentration follows from the condition that the total surface concentration equals the total concentration of active sites, L_t :

$$\sum_{l=1}^{NS} L_l = L_t \quad (7)$$

The set of differential equations (1) and (2) with the boundary conditions (3) and (4) is integrated by means of orthogonal collocation (Finlayson, 1972) solving simultaneously the algebraic equations (5) to (7). The silicon growth rate is obtained from the continuity equation for solid silicon:

$$R_{Si} = \frac{M_{Si}}{\rho_{Si}} \sum_{m=1}^{ns} v_{m,Si} r_{a,m} \Big|_{r=R_0} \quad (8)$$

The outlet molar flow rate of component i , F_i , is obtained by integrating equation (1) over the gas phase reaction volume:

$$F_i = F_{i,o} - \int \int \int \nabla N_i dV + \int \int \int \sum_{k=1}^{ng} \nu_{k,i} r_{v,k} dV \quad (9)$$

It should be stressed that the transport phenomena are completely described by molecular diffusion and, hence, that no adjustable mixing parameters are involved (Villiermaux, 1986; Ottino, 1994).

DETERMINATION OF INTRINSIC KINETICS

In total 210 polysilicon growth rates, and SiH_4 and Si_2H_x outlet molar flow rates obtained with the laboratory reactor were regressed by means of a multi response nonlinear regression algorithm (Marquardt, 1963), using equations (1) to (9) with rate equations corresponding to the reactions listed in

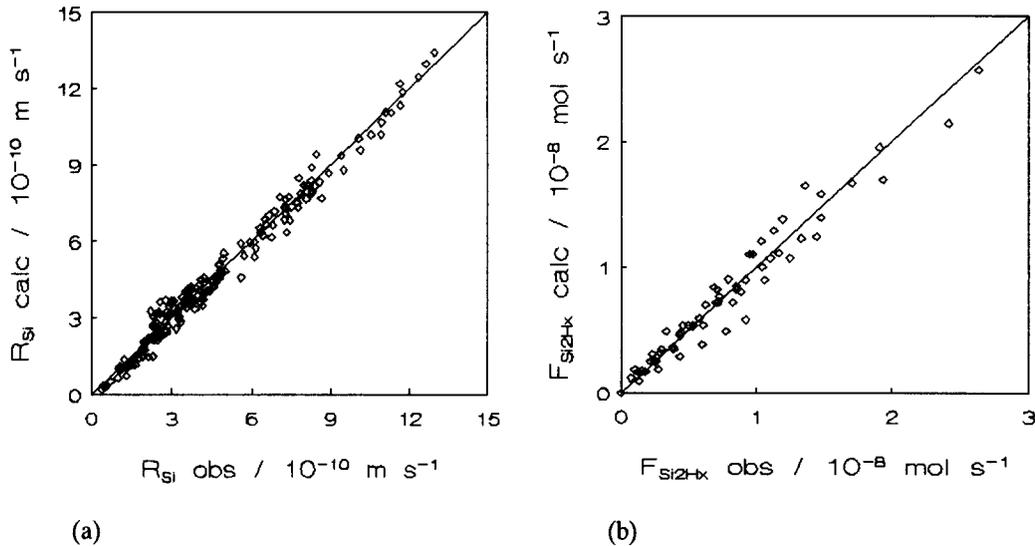


Figure 3a&b Parity diagram. Range of conditions: $p_1 = 25\text{-}125$ Pa, $T = 863\text{-}963$ K, $\text{H}_2/\text{SiH}_4|_0 = 0\text{-}2$, $\text{SiH}_4/\text{Ar} = 0\text{-}7\text{-}9$, $V/F_{\text{SiH}_4,0} = 11\text{-}91$ $\text{m}^3 \text{s mol}^{-1}$. a) Silicon growth rate b) Si_2H_x outlet flow rate.

Table 1 (Weerts, 1995). The calculated Si_2H_x responses were obtained by summarizing the individual calculated outlet molar flow rates of H_3SiSiH , H_2SiSiH_2 and Si_2H_6 . Only five parameters were adjusted during the regression: the frequency factor for the pyrolysis of silane, reaction (1) of Table 1, the frequency factor and the activation energy for the rate-determining step in the desorption of hydrogen adatoms and both the Van 't Hoff parameters for the sorption of molecular hydrogen. Except for the standard entropy for the sorption of molecular hydrogen the obtained estimates were physically reasonable, i.e. within the range of values expected for intrinsic kinetic parameters. Figure 3a shows a parity diagram of the calculated versus the observed polysilicon growth rates. The absence of systematic deviations reflects the adequacy of both the reactor and the rate equations used. Calculated and observed growth rates deviate by less than 15%. The agreement between calculated and observed outlet flow rates of silane is even better. The deviations between calculated and observed outlet flow rates of Si_2H_x components are somewhat larger, typically less than 20%, see Figure 3b. Clearly, the agreement between calculation and experiment with the laboratory reactor is satisfactory. Growth data obtained in a commercial LPCVD reactor can also be described adequately with the developed rate equations, without adjusting any kinetic parameter (Weerts *et al.*, 1996), confirming their reliability and, hence, that of the approach followed in the present work.

CONCLUSIONS

The macromixing in the designed laboratory reactor is completely determined by fast molecular diffusion. Micromixing effects on the gas phase reactions during LPCVD of polycrystalline silicon from silane are absent. The high reaction probabilities of the products of these reactions towards the deposition surface

give rise to significant concentration gradients between the latter and the bulk of the gas phase. Despite these irreducible transport limitations it is possible to obtain intrinsic kinetic data with the experimental set-up. This requires the analysis of the obtained data with a reactor model taking into account the transport limitations in an appropriate way. The latter does only feature binary diffusion coefficients, which can be calculated independently, as transport parameters. Hence, a regression of the experimental data provides estimates of intrinsic kinetic parameters alone.

NOTATION

A_d	total deposition surface area	$1.45 \cdot 10^{-2} \text{ m}^2$
$D_{i,m}$	effective molecular diffusion coefficient of species i in a multicomponent mixture	$\text{m}^2 \text{ s}^{-1}$
$Da_{II,i}$	$= \frac{k_{s,i} R}{D_{i,m}}$, Damköhler II number	-
F	total outlet molar flow rate	mol s^{-1}
$F_{i,o}$	inlet molar flow rate of species i	mol s^{-1}
F_v	volumetric flow rate	$\text{m}^3 \text{ s}^{-1}$
$k_{s,i}$	adsorption rate coefficient for species i	m s^{-1}
$k_{v,i}$	volumetric reaction rate coefficient for species i	s^{-1}
L_i	surface concentration of species i	mol m^{-2}
L_t	total surface concentration of active sites	$1.13 \cdot 10^{-5} \text{ mol m}^{-2}$
N_i	molar flux of species i	$\text{mol m}^{-2} \text{ s}^{-1}$
r	radial coordinate	m
r	reaction rate	reaction dependent
R	radius of reactor	m
R_o	inner radius used in reactor model	$1,396 \cdot 10^{-2} \text{ m}$
R_t	outer radius used in reactor model	$3,097 \cdot 10^{-2} \text{ m}$
V_g	gas phase reaction volume	$1.13 \cdot 10^{-4} \text{ m}^3$
y_i	molar fraction of species i	-
ν	stoichiometric coefficient	-
ϕ_i	$= R \sqrt{\frac{F_v}{V_g D_{i,m}} + \frac{k_{v,i}}{D_{i,m}}}$, modified Thiele-modulus	-

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