Modelling of CVD reactors: thermochemical and mass transport approaches for $\text{Si}_{1-x}\text{Ge}_x$ deposition

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Abstract - Over the years, the design of chemical vapor deposition processes has relied on accumulated empirical ability. It is now well established that the properties of films grown by this chemical process are strongly determined by both transport phenomena and homogeneous and heterogeneous reactions in the reactor. Thermodynamic calculations and mass transport modeling provide a possible approach to delineate the general features of a given process. The application of this concept to the deposition of $\text{Si}_{1-x}\text{Ge}_x$ alloys has led to a better knowledge of the physicochemical phenomena involved in the growth of these materials.

1. - Introduction

$\text{Si}_{1-x}\text{Ge}_x$ alloy films grown by chemical vapor deposition have been used in the production of crystal monochromators [1]. For this process, the use of GeCl_4 and SiH_4 or SiCl_4 mixtures is preferred over that of GeH_4 and SiH_4 mixtures because of the accumulated experience. It is now well established that the properties of films grown by this method are strongly determined by both transport phenomena and homogeneous and heterogeneous reactions taking place in the reactor. The relevant models relate deposition performance (deposition rate and uniformity, film composition, selectivity) to reactor geometry and processing conditions (pressure, temperature, reactant concentration and growth rate) [2-4]. Due to the complexity of the growth chemistry of $\text{Si}_{1-x}\text{Ge}_x$ [1], a modeling effort has been initiated because accumulated experimental data on growth rates and film composition do not provide a satisfactory description of the process.

An *a priori* thermodynamic approach provides an assessment of the experimental method such as the determination of reactant gases and the phases likely to be formed from the initial gas mixture. This approach to complex chemical equilibria involved in multiphase systems is based on the minimization of the global Gibbs' free energy of the system. It has been applied to mixtures of (a) SiH_4 and GeH_4 diluted in Ar (b) SiH_4 and GeH_4 diluted in Ar with small amounts of HCl diluted in H_2 (c) SiH_4 and GeCl_4 diluted in Ar at a high temperature of 1300 K. The results of the theoretical equilibrium study (a) were compared to experimental data (e.g., the stoichiometry of the deposit) obtained in a vertical cold-wall reactor and to the results of a transport model which takes into account the dynamical nature of the process. Through these comparisons, the interactions between mass transport phenomena and coating properties were distinguished and clarified.

2. - Thermodynamic approach

2.1. Thermodynamic data

The thermodynamic calculations were performed by means of Melange software package [5] linked with the SGTE databank [6]. The gaseous species which were taken into account are listed in Table 1. The only solid phase considered was the $\text{Si}_{1-x}\text{Ge}_x$ solid solution.

For the Si-H-Cl system, a coherent set of data is available though complementary measurements for the SiCl_x gaseous species should be made [7]. For the Ge-H-Cl system, all needed data are not available. They were estimated by ponderation methods for GeHCl_3 , GeH_2Cl_2 and GeH_3Cl and by invoking the

similarity in the behaviour of the elements Ge and Si element with respect to H and Cl atoms for the other gaseous species. Table 2 lists the estimated thermochemical data. These methods certainly provide rough values but the gaseous species concerned are of less importance in the relevant experiments. Other gaseous species are generally neglected [1, 7, 9, 10].

SiH ₄	SiH ₃	SiH ₂	SiH	SiCl ₄	SiCl ₃	SiCl ₂	SiCl
GeH ₄	<i>GeH₃</i>	<i>GeH₂</i>	<i>GeH</i>	GeCl ₄	GeCl ₃	GeCl ₂	GeCl
Si ₂ H ₆	Si ₂ Cl ₆	Si ₁	SiHCl ₃	SiH ₂ Cl ₂	SiH ₃ Cl		
Ge ₂ H ₆	Ge ₂ Cl ₆	Ge ₁	<i>GeHCl₃</i>	<i>GeH₂Cl₂</i>	<i>GeH₃Cl</i>		

Table 1 : Gaseous species used in the model (thermodynamic data of gaseous species written in italic were estimated).

	ΔH_{298}	S_{298}	A	B	C	D
GeH	3.0355E+5	2.1299E+2	2.9124E+1	7.2249E-3	-2.4130E-7	3.4411E+6
GeH ₂	2.3263E+5	2.2200E+2	4.0327E+1	1.2347E-2	-1.6269E-7	1.5737E+6
GeH ₃	1.6171E+5	2.2999E+2	5.1531E+1	1.7232E-2	-8.4219E-8	-2.9369E+5
GeHCl ₃	-3.5230E+5	3.2900E+2	9.5814E+1	6.1010E-3	1.5529E-8	-1.2832E+6
GeH ₂ Cl ₂	-2.0460E+5	3.0199E+2	8.4788E+1	1.1439E-2	8.4630E-9	-1.5758E+6
GeH ₃ Cl	-5.6910E+4	2.6599E+2	7.3761E+1	1.6777E-2	1.3963E-9	-1.3732E+6

Table 2 : Estimated thermochemical data of the Ge-H-Cl system
($C_p = A + BT + CT^2 + DT^{-2}$ in J.mol⁻¹).

For the Gibbs' free energy description of the Si-Ge solid solution, we have used the recent values published by C. Bergman et al. [8]. For the strictly regular solid solution, the excess Gibbs' free energy is given by :

$$\Delta G^{xs} = 3500 X_{Ge} X_{Si} \quad (\text{J.mol}^{-1})$$

where X_i is the molar fraction of species i in the solid phase.

2.2. CVD simulation

Thermodynamic calculations require the knowledge of total pressure, temperature, argon dilution if necessary, Y_{Ge} and Cl/H. The quantity Y_{Ge} is defined as the ratio of the inlet molar fraction of gaseous species containing germanium over the inlet molar fraction of gaseous species containing germanium and silicon. The quantity Cl/H is defined as the ratio of the number of Cl atoms over the number of H atoms introduced in the reactor.

The first thermodynamic calculations for the Si-Ge-HCl system at atmospheric pressure were performed by Anderson et al. [9]. More recently Tang et al. [10] have determined the thermochemical equilibrium at low pressures for the SiH₂Cl₂-GeH₄-H₂ and the SiCl₄-GeCl₄-H₂ systems. In order to check the validity of our set of thermodynamic data, we have compared our equilibrium calculations with those of Tang et al. [10]. Even though slight discrepancies have been observed, like for example, the presence of gaseous SiCl₃ at equilibrium, a species not taken into account by Tang et al. [10], good agreement is obtained between the two sets of results as illustrated in Figure 1.

The pressure, temperature and Y_{Ge} ranges investigated are, respectively, 10² to 10⁵ Pa, 600 to 1400 K and 0 to 1 for an initial mixture of GeH₄ and SiH₄ diluted (from 1 to 3%) in Ar.

In all cases, the simulation has provided identical values of X_{Ge} and Y_{Ge} because the amounts of silicon and germanium in the gas phase are very small. The situation will be quite different if more stable gaseous species containing Ge and Si like the chlorides are used. We have modeled two types of experiments ; in the first small amounts of HCl were introduced in the Ar-GeH₄-SiH₄ mixture and in the second, a mixture of Ar-GeCl₄-SiH₄ was used. Figure 2 represents the evolution of the germanium fraction in the solid, X_{Ge} , as a function of temperature, for different gaseous mixtures and for different germanium fraction, Y_{Ge} , in the inlet mixture. For the two mixtures investigated, the general trends are similar (Fig. 2). When HCl is used, the Cl/H ratio is small and fixed. In this case only an effect of

temperature is observed ; the Y_{Ge} - X_{Ge} gap is slightly increased as the temperature increases for the higher values of Y_{Ge} . When $GeCl_4$ is used, the Cl/H ratio varies and is equal to Y_{Ge} . In this case, the Y_{Ge} - X_{Ge} gap increases with temperature and the Cl/H ratio.

As a partial conclusion, this *a priori* modeling approach showed that at 133 Pa the important parameters for the control of the Ge fraction in the coating are the Cl/H ratio and the temperature. At atmospheric pressure, the modeling results are quite different [9-10].

X_{Ge} (%)

Fig. 1. - Evolution of X_{Ge} (for $Y_{Ge} = 0.2$) in the deposit as a function of pressure at 1300 K. Curves 1 and 2 are calculated by Tang et al. [10] respectively for the SiH_2Cl_2 - GeH_4 - H_2 and $SiCl_4$ - $GeCl_4$ - H_2 systems ; the points marked by Δ , O are calculated in the present study.

X_{Ge} (%)

Fig. 2. - Evolution of X_{Ge} as a function of the temperature for different Y_{Ge} values and different gaseous mixtures ($P = 133$ Pa).
 — Ar (99%) - SiH_4 + $GeCl_4$ (1%) $Cl/H = Y_{Ge}$
 - - - Ar (95%) - SiH_4 + GeH_4 (1%)
 H_2 + HCl (4%) with HCl (0.04%)
 $Cl/H = 0.25 \times 10^{-2}$

3. - Experimental results

Previous studies [1, 11-12] have shown that, as usual, for different initial gaseous mixtures leading to $Si_{1-x}Ge_x$ deposition, in the low temperature range (< 1173 K), the deposition rate increases with the temperature and is limited by surface chemical kinetics. In the high temperature range, the deposition rate remains almost constant and is mainly limited by the reactive gas transport. On the other hand, more specific observations have been performed [1, 11-13]. In the low pressure (800 Pa) and temperature (973 K) ranges, the deposition rate of $Si_{1-x}Ge_x$ from mixtures of germane (GeH_4) and dichlorosilane (SiH_2Cl_2) is increased compared to silicon deposition alone (with SiH_2Cl_2) [11]. The same phenomena are observed when atmospheric pressure and a higher temperature of 1173 K are used [12]. When GeH_4 , SiH_4 and HCl are used at atmospheric pressure, the deposition rate of $Si_{1-x}Ge_x$ as a function of temperature is identical to that of silicon [13]. Finally the addition of small amounts of HCl ($Cl/H = 0.5 \times 10^{-2}$) to the GeH_4 , SiH_4 and Ar mixture lead to a X_{Ge} fraction of 0.79 [1]. The thermodynamic calculations performed have not explained this discrepancy. These last experimental results [1] have been performed with the same reactor as that used in the present study.

In this reactor a GeH_4 - SiH_4 gas mixture streams over a heated silicon substrate. The GeH_4 and SiH_4 which contact the hot surface crack, freeing silicon or germanium atoms for epitaxial deposition onto the substrate. The germanium concentration of the crystal depends on the germane concentration in the gas mixture, which is easily controlled. Figure 3 shows a sketch of the LPCVD furnace. A quartz plate, 150 mm in diameter, holds the silicon wafer (100 mm) which is located inside a water-cooled stainless steel

vessel (diameter = 300 mm ; height = 300 mm). The substrate is heated from below by a graphite resistor.

A thermocouple placed near the wafer monitors the process temperature. The actual temperature (1300 K) during deposition was calibrated during deposition of pure silicon.

The experimental results obtained without HCl ($Y_{Ge} = 25\%$) are plotted on figure 4 together with the results obtained with small amounts of HCl [1]. In both cases, we observed the same X_{Ge}/Y_{Ge} ratio. Thermodynamic equilibrium calculations (see section 2.2) show indeed that the introduction of small amounts of HCl (0.04%) leads to a slight decrease in the germanium content of the deposited layer (curve 2 in Fig. 4) compared with the result obtained without HCl (curve 1 in Fig. 4). The experimental results obtained with HCl [1] and without HCl are however far below the calculated values. These results suggest that mass transport phenomena could be of importance during the deposition process.

Fig. 3. - Schematic of the CVD reactor.

Fig. 4. - Evolution of the germanium ratio in the deposit as a function of germane ratio (Y_{Ge}) in the gas phase : curve 1, results of the thermodynamic calculations without HCl. ; curve 2, results of the thermodynamic calculations with HCl; experiments (with Δ or without $\blacktriangle$ small amounts of HCl).

4. - Mass transport modeling

The CVD process involves momentum, mass, energy and species balances [14]. The general derivation and form of these equations are given in standard references on transport phenomena [15]. The general finite element code Flux Expert was adapted to solve some CVD problems [16]. The model assumes steady state conditions, laminar flow and the validity of the ideal gas law. In the energy equation the heat of reaction from gas phase reactions, the viscous dissipation and the radiant heat transfer were neglected. The flow and energy equations are coupled to the species balance equations. Three species have been taken into account : Ar, SiH_4 , GeH_4 . Homogeneous reactions have been ignored, i.e., intermediate bulk gas phase products have the same reaction probabilities and the same transport properties as the inlet gases. The boundary conditions are, (i) no slip was assumed at the walls, the inlet profile was parabolic and a zero gradient was prescribed for the exit velocity, (ii) the temperatures were specified for the walls and the substrate, and at the exit, a zero gradient was imposed, (iii) the concentrations of the gas species were prescribed at the inlet area, a zero diffusion flux on the non-reacting areas, (iiii) on the reactive substrate, a kinetic or diffusional limitation can be selected. In the absence of experimental data, the transport properties of the gas species and the gas mixtures were calculated from kinetic theory. This has already been discussed [17]. The reactor was assumed to be axisymmetric and the geometry of the

experimental reactor was slightly simplified (Fig. 5a); the validity of these simplifications have been checked through computations.

The model predicts the flow velocities, the temperature and the concentration fields and the composition of the deposit as a function of its location in the reactor (Fig. 5b and c). As it was predicted by a dimensionless analysis, the buoyancy forces do not influence the flow. Figure 6a shows the total fluxes of silane and germane at the substrate calculated assuming a mass transport limitation (all SiH_4 and GeH_4 are consumed at the substrate) for the reacting gases. The stoichiometry of the deposit (Fig. 6b) is calculated by :

$$X_{\text{Ge}} = \frac{J_{\text{GeH}_4}}{J_{\text{GeH}_4} + J_{\text{SiH}_4}}$$

Fig. 5. - (a) Simplified axisymmetric geometry used for the simulations. One half of the reactor will be used to present the results of the model.

(b) Calculated velocity and (c) temperature fields in the cold-wall axisymmetric reactor for an inlet flow of 2 l/min (STP) of Ar - 0.5% SiH_4 - 0.5% GeH_4 at 300 Pa; the substrate temperature is 1300 K (one half of the reactor is shown). The same features are observed when varying the SiH_4 and GeH_4 fractions from 0 to 1% and when varying the temperature.

Fig. 6. - (a) Total fluxes of silane (---) and germane (—) calculated along the substrate (at the center the calculated deposition rate is $0.6 \mu\text{m}/\text{min}$).
 (b) calculated stoichiometry of the deposit along the substrate (The experimental conditions are the same as in figure 5).

Fig. 7. - Comparison between the experimental and modeling results obtained for the stoichiometry of the deposit. Curve 1 : thermodynamic modeling ; curve 2 : mass transport modeling ; Δ experimental results (with HCl Δ ; without HCl $\blacktriangle$).

Although the fluxes of the reactive species vary along the substrate, the value of X_{Ge} remains almost constant along the substrate.

Figure 7 shows the comparison between the model and the experimental results. The use of a mass transport model gives results (curve 2) closer to experimental values than previous thermodynamic calculations (curve 1). The mass transport model should be improved by using more sophisticated chemical kinetic data, but these are missing. Advanced modeling, linking thermodynamic and mass transport approaches to obviate the lack chemical kinetic data, will not lead to better fit for small amounts of HCl but will be of great interest for reactive mixtures with high Cl/H ratios. This work has been initiated.

5. - Conclusion

Experimental and theoretical approaches were performed for the deposition of $Si_{1-x}Ge_x$ in a vertical cold-wall reactor. When SiH_4 and GeH_4 gaseous species, with or without small amounts of HCl, diluted in Ar are used, the thermodynamic modeling alone is not able to predict correctly the chemical phenomena involved during deposition. On the other hand, mass transport modeling seems to evidence that deposited fluxes are of importance for the resulting composition of the coating, even if simplified chemical kinetic data have are used. Due to the prohibitive cost of GeH_4 for long-lasting experiments, chlorine sources ($GeCl_4$) are preferred to GeH_4 . For this system, the thermodynamic model predicts important gaps between X_{Ge} and Y_{Ge} . In this case, and in order to better describe the entire chemical process, it is of interest to link the thermodynamic calculations with mass transport calculations in the absence of data on chemical kinetics. This coupled approach, fully supported by experiments, is in progress and appears to be a possible modeling route which would provide more accurate information on the fundamental processes operating during chemical vapor deposition.

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