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Kinetic Modeling of the Gas Phase Decomposition of Germane by Computational Chemistry Techniques

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Abstract. Very limited experimental data are available on thermal decomposition of germane in the gas phase. Recent developments in theoretical quantum chemistry techniques such as *ab initio* Hartree-Fock and density functional methods have made accurate determination of molecular properties possible. Systematic development of a detailed gas-phase decomposition mechanism for germane using *ab initio* molecular orbital calculations is described in this work. A decomposition pathway for germane and higher germanes is proposed and the relevant reaction rates are calculated using transition state theory combined with unimolecular and chemical activation treatments. The decomposition model is implemented into a realistic thermal-fluid simulation.

1. INTRODUCTION

Si_{1-x}Ge_x alloys have recently attracted considerable attention as a material for manufacturing high speed electronic devices like high-electron mobility transistors (HEMT's) and heterojunction bipolar transistors (HBT's) or various optoelectronic devices. The composition of the deposited Si_{1-x}Ge_x alloys strongly affects device performance. Controllability of composition as well as of film thickness is one of the key limitations in wafer processing. Hence, the knowledge of epitaxial growth kinetics is very important, especially as device dimensions continue to reduce.

Very limited experimental data exist for the gas-phase pyrolysis of GeH₄. In this work *ab initio* molecular orbital (MO) calculations [1] are applied to GeH₄ decomposition. Heats of formation of the relevant species and transition state configurations are calculated and reaction barriers for several possible reactions are predicted. The reaction rates for the most probable decomposition pathway are calculated using conventional transition state theory combined with unimolecular and chemical activation treatments. The agreement between calculated and measured reaction rates is found to be very good. The importance of the individual reactions of the decomposition path is evaluated by thermal-fluid simulations in a realistic reactor geometry.

2. AB INITIO CALCULATIONS

All molecular properties of a given molecule can in principle be calculated by solving the Schrödinger equation (in Dirac notation)

$$\mathcal{H} | \Psi \rangle = E | \Psi \rangle \quad (1)$$

where \mathcal{H} is the Hamiltonian describing the total energy of the system and Ψ is the many-particle wave-function which depends on the coordinates and spins of all n particles

$$| \Psi \rangle = | \Psi (\vec{r}_1, \omega_1, \vec{r}_2, \omega_2, \dots, \vec{r}_n, \omega_n) \rangle \quad (2)$$

The mathematical difficulties involved in solving the Schrödinger equation make it impossible to attempt an exact solution even for small molecules. The Born-Oppenheimer approximation allows a separate treatment of electronic and nuclear motions. The Hartree-Fock approximation replaces repulsion between individual electrons by an average potential of all electrons. The now simplified time independent Schrödinger equation states an eigenvalue problem. The variational method determines the minimal energy wave function $|\Psi'\rangle$ which is the best estimate to the exact solution. In general $|\Psi'\rangle$ will be such a complicated function that there is no simple way to find the energy minimum. However, if only linear variations of the trial function are allowed, i.e.

$$|\Psi'\rangle = \sum_{i=1}^n c_i |\Phi_i\rangle, \quad (3)$$

with $\{|\Phi_i\rangle\}$ being a set of fixed basis functions, then finding the optimum set of coefficients c_i is reduced to a matrix diagonalization problem.

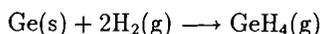
In the Hartree Fock (HF) approximation each electron pair is assigned its own orbital and interelectronic repulsion is treated in an average way. Physically, electrons do not obey a static distribution but interact with each other instantaneously. The most common method to improve HF wave-functions in this respect and to correct for electron correlation effects is applying Møller-Plesset (MP) perturbation theory or configuration interaction (CI) [2].

2.1 Used methodology

MO theory is used to calculate the molecular properties of individual Ge species from first principles. The calculations are performed at restricted Hartree Fock (RHF) and unrestricted Hartree Fock (UHF) level using the software GAMESS [3]. The theoretical equilibrium geometries and harmonic vibrational frequencies are determined at the HF/BC(2p,3d) level of theory (Hartree-Fock theory using the BC(2p,3d) basis set [4]). Frequencies computed at HF level of theory are systematically larger than the corresponding experimental values. This systematic deficiency is corrected by scaling the vibrational frequencies by a factor of 0.89 [1]. The energy calculations are performed at MP2/BC(2p,3d) and MP2/BC(1d,1f) level (second order Møller-Plesset perturbation theory using the BC(2p,3d) and BC(1d,1f) basis sets) based on the HF/BC(2p,3d) geometries. No bond order correction factors for Ge-H or Ge-Ge bonds are introduced.

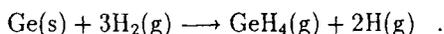
The accuracy of *ab initio* MO calculations depends largely on the size of the chosen basis set, the quality of the basis set in regard to the molecules to be investigated and the level of theory to correct for correlation effects. More accurate calculations significantly increase calculation time. CI, even with a minimal basis set, is computationally expensive for heavier molecules. MP perturbation theory can be applied at different orders. Higher order means better accuracy but also increased calculation time. We chose a high quality basis set together with second-order MP perturbation theory to limit the computational effort but still obtain results with sufficient accuracy for CVD simulations.

In general, heats of formation, ΔH_f^0 , are calculated by subtracting the total energy of the given species at reference state from the equilibrium total energy, e.g.



$$\Delta H_{f,\text{GeH}_4(\text{g})}^0 = E_{\text{tot,GeH}_4(\text{g})} - E_{\text{tot,Ge(s)}} - 2E_{\text{tot,H}_2(\text{g})} + \Delta H_{\text{sub,Ge(s)}}^0 \quad (4)$$

where E_{tot} is the sum of electronic, vibrational, rotational and translational energy and $\Delta H_{\text{sub,Ge(s)}}^0$ is the standard sublimation enthalpy of solid Ge [5]. In the reaction expression (4), the number of valence electron pairs on the product side is larger than on the reactant side. Consequently, the correlation energy is not balanced, which introduces systematic errors. The isogyric approach [1] is used to minimize this effect



Molecule	Heats of Formation ΔH_{fo}^0 [kcal/mole]			
	BC(2p,3d)	BC(1d,1f)	Theory ^a	Experiment
GeH ₄	12.9	17.8	16.8 (19.6)	$\leq 21.7^b$
GeH ₃	47.5	51.3	50.0 (52.8)	$\leq 58.1^c, 54.7 \pm 2^c, 55.2 \pm 2^d, 50.6^e$
GeH ₂ (¹ A ₁)	56.7	57.5	56.4 (59.2)	$\geq 59.3^c, 61.9^c, 60.4 \pm 3.8^d$
GeH ₂ (³ B ₁)	80.0	83.3	82.0 (84.4)	
GeH	75.7	75.7	74.9 (76.0)	$\leq 86.0^c, 76.8^c$
Ge ₂ H ₆	22.0	30.2		$\leq 38.8^b$
HGeGeH ₃		68.6		
H ₂ GeGeH ₂		67.9		

Sublimation Energy of Ge: 88.2 kcal/mole^c
Dissociation Energy of H₂: 103.3 kcal/mole^f

^aR.C. Binning, L.A. Curtiss, *J. Chem. Phys.*, **92**, 2, 1860, (1990)

Values in parentheses include estimates of spin-orbit corrections.

^bCRC Handbook of Physics and Chemistry, *The Chemical Rubber Company*, **73**, (1993)

^cB. Ruscic, M. Schwarz and J. Berkowitz, *J. Chem. Phys.* **92**, 1865 (1990)

^dP.N. Noble and R. Walsh, *Int. J. Chem. Kinetics*, **15**, 547 (1983)

^eB.S. Agrawala and D.W. Setser, *J. Chem. Phys.* **86**, 5421 (1987)

^fJANAF Thermochemical Tables, *Natl. Stand. Ref. Data Ser.*, NIST

Table 1: Comparison of calculated vs measured and predicted heats of formation.

Here the number of electron pairs on the right-hand side and the left-hand side is balanced. The heat of formation of GeH₄ is calculated according to

$$\Delta H_{f,GeH_4(g)}^0 = E_{tot,GeH_4(g)} + 2E_{tot,H(g)} - E_{tot,Ge(g)} - 3E_{tot,H_2(g)} - BDE_{H_2(g)} + \Delta H_{sub,Ge(s)}^0 \quad (5)$$

with $BDE_{H_2(g)}$ being the experimental bond dissociation energy of H₂ [6].

2.2 Results and discussion

Heats of formation for several Ge species calculated with the BC(2p,3d) and the BC(1d,1f) basis set at a reference state of 0K are listed in table 1 along with recently calculated values of Binning and Curtiss (MP4/962(d,p)) [4] and available experimental data. The uncertainty of the calculated numbers is estimated to be around 4 kcal/mole. This includes a general estimated uncertainty of $\approx 2-3$ kcal/mole associated with the accuracy of the HF/MP2 calculations and the uncertainties in the sublimation energy of Ge and the bond dissociation energy of H₂. Calculated heats of formation for the BC(1d,1f) basis set are much closer to the experimental values and Binning and Curtiss' theoretical predictions than are those for the BC(2p,3d) basis set. The BC(1d,1f) calculations are much closer to the HF limit which is the best value for the minimum energy.

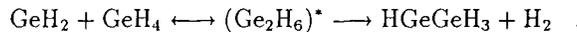
Predicted heats of formation for species with only one Ge atom agree very well with experimental data and the MP4 calculations of Binning and Curtiss. For species with two Ge atoms there is only the experimental heat of formation for Ge₂H₆ available [6]. The discrepancy between this value and the one predicted cannot be attributed solely to uncertainties in the calculations. The problem could be due to deficiencies of the BC(1d,1f) basis set which might properly describe a Ge-H bond but not the Ge-Ge bond.

The predicted reaction barriers are displayed in table 2. It is energetically more favourable for GeH₄ to lose H₂ in an initial decomposition step rather than H, since the latter reaction requires a more than 30 kcal/mole higher activation energy. Reactions involving hydrogen radicals, i.e. GeH₄ + H \rightarrow GeH₃ + H₂ or GeH₃ + H \rightarrow GeH₂ + H₂, have very low activation barriers. However,

Reaction	Reaction Barriers E_0 [kcal/mole]			
	forward barrier		reverse barrier	
	BC(2p,3d)	BC(1d,1f)	BC(2p,3d)	BC(1d,1f)
$\text{GeH}_4 \longrightarrow \text{GeH}_2 + \text{H}_2$	56.6	55.3	13.4	16.2
$\text{GeH}_4 \longrightarrow \text{GeH}_3 + \text{H} (^1A_1)$	89.9	89.0	4.1	3.8
$\text{GeH}_4 \longrightarrow \text{GeH}_3 + \text{H} (^3B_1)$	92.2	91.6	6.3	6.5
$\text{GeH}_4 + \text{H} \longrightarrow \text{GeH}_3 + \text{H}_2$	5.6	6.2	22.9	24.9
$\text{GeH}_3 + \text{H} \longrightarrow \text{GeH}_2 + \text{H}_2$	5.4	6.1	48.1	52.2
$\text{GeH}_4 + \text{GeH}_2 \longrightarrow \text{Ge}_2\text{H}_6$		≈ 0		44.5
$\text{Ge}_2\text{H}_6 \longrightarrow \text{HGeGeH}_3 + \text{H}_2$		49.6		11.7
$\text{HGeGeH}_3 \longrightarrow \text{H}_2\text{GeGeH}_2$		9.9		10.6

Table 2: Calculated reaction barriers.

the hydrogen radical concentration in the gas phase is close to zero for typical CVD conditions so that these reactions can be neglected. GeH_2 can react with GeH_4 without additional activation. The resulting $(\text{Ge}_2\text{H}_6)^*$ is vibrationally energized. It can either undergo collisional stabilization, react via a chemically activated pathway to form HGeGeH_3 and H_2 , or react along the original pathway to re-form the reactants. The chemically activated channel



extends the decomposition pathway to the formation of HGeGeH_3 and H_2GeGeH_2 . HGeGeH_3 isomerizes with an activation barrier of about 10 kcal/mole to form H_2GeGeH_2 . The outlined decomposition path is visualized in figure 1. The activated channel represents a 'short cut' on the sketched energy surface. The proposed decomposition pathway for GeH_4 is similar to SiH_4 decomposition [7,8 and references within].

3. RATE CONSTANTS

Transition state theory (TST) is widely used to interpret or estimate rate data. TST requires no calculations on the dynamics of the reacting system. A characteristic of unimolecular reactions is the dependence of the rate constant on collisional energy transfer. This results in a direct dependence of the overall rate constant on the pressure of the bath gas. The application of TST to unimolecular reactions results only in the rate constant at the high pressure limit, k_{uni}^∞ . It does not allow the estimation of the pressure dependence of the unimolecular rate constant, $k_{uni}(p)$. Other techniques like Rice-Ramsperger-Kassel-Marcus (RRKM) treatment or Quantum-Rice-Ramsperger-Kassel (QRRK) analysis must be considered.

RRKM theory is based on two major assumptions: (1) the existence of a critical geometry as required for TST and (2) the ergodicity hypothesis. The ergodicity hypothesis states that intramolecular energy transfer is rapid compared to reaction. The program that has been used in this work for performing the RRKM calculations is the UNIMOL program suite by Gilbert *et al.* [9]. UNIMOL provides the biased random walk (BRW) model for calculating the collisional energy transfer. The Lennard-Jones parameters for the Ge species, required for the RRKM calculations, are calculated according to the procedures outlined by Coltrin and coworkers [10]. The rate coefficient for the reverse recombination reaction, k_{rec} , can be obtained from the forward rate, k_{uni} , and the equilibrium constant.

The calculation of the rate constant for reaction systems involving a chemically activated channel is determined by competition among all possible reactions: i) stabilization by collisions, ii) redissociation into reactants and iii) formation of new products by dissociation or isomerization. The analysis

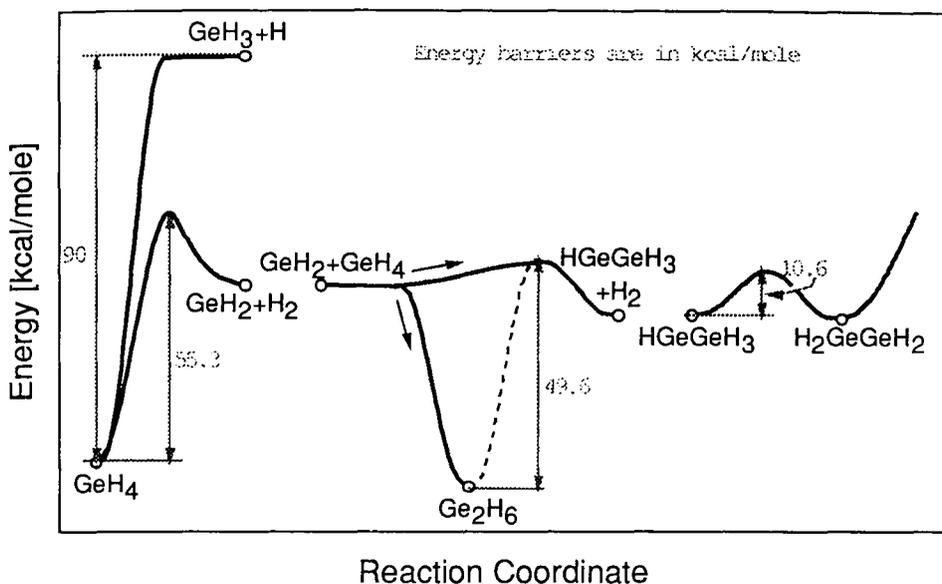


Figure 1: Energetics of major decomposition path

by RRKM methods for this type of reaction system is very complicated and not yet fully developed. Therefore, the QRRK method proposed by Dean and Westmoreland [11] in similar combustion reactions is applied. Predictions of rate constants by QRRK need only very few molecular structure and thermodynamic data; no transition state parameters are required.

3.1 Discussion of predicted rate constants

Figure 2 shows predicted falloff curves for the decomposition of GeH_4 into GeH_2 and H_2 at temperatures of 800 K, 1000 K and 1200 K. The falloff curves have been generated using RRKM analysis. Ring, O'Neal and coworkers have investigated this reaction by means of shock tube experiments [12]. At a pressure of 4000 torr and temperatures around 1000 K they measured a rate constant of $\log k_{\text{GeH}_4,4000} = 13.83 \pm 0.78 - 50750 \pm 3750\text{cal}/2.303RT$. They estimated the high pressure rate constant by fitting RRKM calculations to their data to $\log k_{\text{GeH}_4,\infty} = 15.5 - 54300\text{cal}/2.303RT$. Their high pressure limit is in good agreement with the $\log k_{\text{GeH}_4,\infty} = 15.5 - 52100\text{cal}/2.303RT$ reported by Votintsev and coworkers [13]. Our theoretical calculations result in a pressure independent activation energy of $E_a(T = 1000\text{K}) = 56.2 \text{ kcal/mole}$. The predicted rate constants are $\log k_{\text{GeH}_4,4000} = 13.6 - 56.2\text{kcal}/2.303RT$ and $\log k_{\text{GeH}_4,\infty} = 14.3 - 56.2\text{kcal}/2.303RT$. These rate constants are slightly lower than the ones reported by Ring, O'Neal and coworkers; however, our predicted $k_{\text{GeH}_4,4000}$ is still inside the error limits of the measurement. Su and Schlegel calculated the high pressure rate constant for unimolecular decomposition of SiH_4 into SiH_2 and H_2 from *ab initio* calculations [14]. Similar to our result they compute a pre-exponential factor an order of magnitude smaller than the experimentally derived value. They attribute this difference to a small exit barrier and a strongly bound complex, which means that the silane decomposition should be treated by a variational transition state approach. A similar conclusion was drawn by Moffat *et al.* [8] in the analysis of a large number of experimental studies.

The GeH_2 created by elimination of H_2 from GeH_4 further reacts with GeH_4 . This reaction branches the decomposition path into i) stabilization of the activated $(\text{Ge}_2\text{H}_6)^*$ and ii) activated dissociation to form HGeGeH_3 and H_2 . The rate constants for stabilization and activated dissociation have been calculated by the QRRK method. The results are displayed in figure 3. The rate constant

of the chemically activated channel is pressure independent according to the bimolecular character of the reaction. Unimolecular stabilization of $(\text{Ge}_2\text{H}_6)^*$ increases linearly with respect to pressure in the low pressure regime. The activated channel dominates over stabilization at high temperatures and low pressures.

The stabilized Ge_2H_6 also forms HGeGeH_3 and H_2 . This reaction is embedded in the reaction network associated with the activated decomposition of excited $(\text{Ge}_2\text{H}_6)^*$. The rate constants are therefore estimated using the QRRK technique. HGeGeH_3 isomerizes into H_2GeGeH_2 . The activation energy for the isomerization is low, $E_a = 9.9$ kcal/mole. Hence, if HGeGeH_3 is formed, it would be expected to readily isomerize into H_2GeGeH_2 .

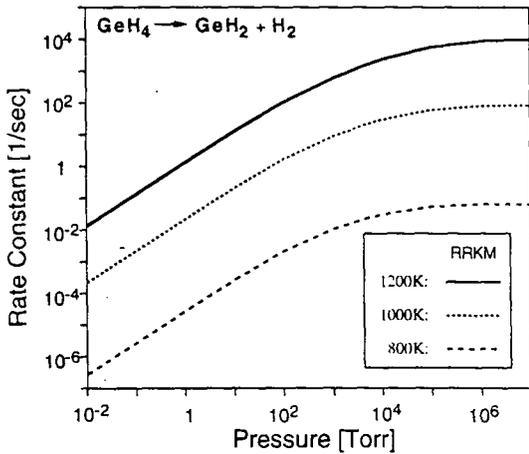


Figure 2: Rate constants for unimolecular decomposition of GeH_4 .

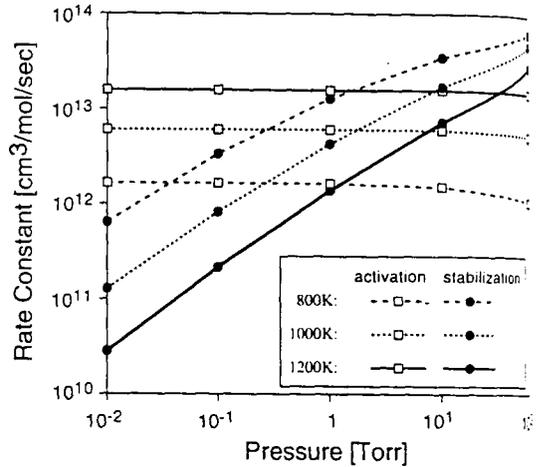


Figure 3: Comparison of rate constants for the activation and stabilization reactions.

4. CVD SIMULATIONS

The developed kinetic model for gas-phase pyrolysis of GeH_4 is implemented into a realistic thermal fluid simulation of an existing CVD reactor. The reactor is described elsewhere [15]. For the present studies the reactor is modeled as being isothermal. Typical process conditions are assumed: the flow rate is 1000 sccm H_2 with 10 sccm GeH_4 , the temperature is between 800 K and 1000 K and the pressure varies from 1 torr to 10 torr.

There is basically no decomposition of GeH_4 at a temperature of 800 K and a pressure of 1 torr. This result is not surprising since the activation energy for the initial decomposition step is quite high, $E_a = 56$ kcal/mole. The abundance of H_2 promotes the reverse reaction and therefore inhibits decomposition further. The mole fractions of decomposition products in the reactor are about five orders of magnitude lower than the GeH_4 mole fractions. Increasing the temperature to 1000 K at 1 torr introduces a weak initial decomposition of GeH_4 . Still the amount of GeH_4 decomposed is less than 1%. The generated GeH_2 immediately reacts with GeH_4 to form Ge_2H_6 and HGeGeH_3 . The mole fractions of HGeGeH_3 or H_2GeGeH_2 are one order of magnitude higher than the ones of Ge_2H_6 . This indicates that the activated channel dominates stabilization of $(\text{Ge}_2\text{H}_6)^*$.

At a pressure of 10 torr decomposition increases significantly at all temperatures. For $T = 1000$ K the GeH_4 inlet mole fraction is reduced 15% in the reactor. Again the reaction of GeH_2 with GeH_4 is very fast (the mole fractions of GeH_2 are 1 to 2 orders of magnitude lower than the ones of the other pyrolysis species). The significant difference from the 1 torr simulations is the ratio of Ge_2H_6 (the stabilized species) to HGeGeH_3 and H_2GeGeH_2 (the products of the activated channel). The mole fractions of all these species are in the same order of magnitude, indicating that the activated channel is not dominating stabilization any more. Activation and stabilization are both important.

Gas phase decomposition of germane and higher germanes is significant in CVD at temperatures above 800 K and pressures above 10 torr. In modeling approaches it is important to include not only the initial decomposition of GeH₄ but to extend the kinetic model to higher germanes. Analogous to the silane system the higher germanes are potentially more efficient for Ge film deposition since with each precursor molecule multiple Ge atoms adsorb on the surface.

5. CONCLUSIONS

Computational chemistry is capable of closing the gap between the availability of experimental data and the need for kinetic information in modeling microelectronics deposition processes. Quantum chemistry techniques deliver thermochemical properties in good agreement with measured quantities. A careful selection of the basis set and the inclusion of the major correlation corrections using second-order MP perturbation theory gives sufficiently accurate results and keeps calculation time inside reasonable limits. This makes quantum chemistry techniques attractive not only for the academic community but also for engineering applications. The thermochemical data can be interpreted by TST, RRKM and QRRK calculations to predict rate constants. The developed kinetic model can easily be implemented in a thermal-fluid simulation of a given CVD reactor.

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