

Joint Russian and Bulgarian Academies of Sciences Database of Intermolecular Potentials and Diffusion Coefficients for Components of the CVD Processes in Microelectronics¹

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The goal of the database (DB) EPIDIF-JRB is to promote the modeling of gas-phase transport processes in CVD technologies in microelectronics. The transport properties (molecular diffusion coefficients, viscosity, and thermal conductivity) of pure gases and gas mixtures in the temperature range 250 to 2000 K and at a pressure < 0.1 MPa are calculated using (1) the Chapman–Enskog method in binary collision approximation and (2) the three-parameter Lennard–Jones ($m-6$) intermolecular potentials (IP) with $8 < m < 100$ for interactions of atoms and quasi-spherical molecules, and (3) the four-parameter $m-6-3$ Stockmayer IP for dipole molecules. In addition to the IP parameters a_{ii} , a_{jj} , and a_{ij} , the DB also supplies their variance–covariance matrix. For heavy globular molecules [such as CF_4 , SiH_4 , $\text{Si}(\text{CH}_3)_4$, and WF_6], the influence of the vibrational excitation on their effective size is considered. In this case, the isotropic Lennard–Jones ($m-6$) IP with temperature-dependent parameters was defined. At present, the DB EPIDIF-JRB contains 40 species of importance to Si gas-phase epitaxy processes and IP parameters for 820 pair interactions. It can be used to calculate the viscosity of pure gases and gas mixtures with any k components ($k < 11$), and their binary diffusion coefficients, and to estimate their uncertainty as well.

KEY WORDS: CVD processes; database; diffusion coefficients; gas viscosity; intermolecular potentials; silicon epitaxy.

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1. INTRODUCTION

The processes of producing substances by means of the gas-phase transport of the components [chemical vapor deposition (CVD) processes] occupy an important place in contemporary materials science. They are a part of advanced technologies which allow control of the purities and the structure of the crystal, e.g., the material properties.

Such an approach has been used to obtain many classes of substances: semiconductors of a high purity (Si, Ge, etc.), compounds of elements of different groups (II-VI, III-V, etc.) which create Si-like structures; metals (Cu, Pt, W, Mo, Ti, Zr, etc.), thin oxide films (SiO_2 , Al_2O_3), carbides, nitrides, and high-temperature semiconductors such as $\text{YBa}_2\text{Cu}_3\text{O}_7$. The number of such substances is many hundreds. For example, in one of the first monographs on CVD, the author mentioned 118 transported species [1]. The number is now perhaps 10 times larger. (Note that the number of abstracts on the subject "Vapor Deposition Processes" in *Chemical Abstracts* for the first half of 1995 was about 2500.)

One has to remember that each expected substance requires two or three transported agents (precursors)—organic or organometallic substances. These precursors, as a rule, have to be dissolved in a medium of gas carriers (H_2 , He, N_2 , etc.). Therefore, intermediate species could also appear in the gas phase. These particles will participate in the mass transport process toward the substrate, and some of them will return to the gas volume.

It is obvious that modeling of CVD processes in semiconductor microelectronics requires knowledge of the thermophysical properties of many thousands of substances. Therefore, the organization of information and data for CVD process calculations has become a task of worldwide interest.

Current CVD processes usually take place at temperatures from 500 to 1700 K and at pressures $p < 0.1$ MPa. Under these conditions, the gas-phase thermodynamic properties are described by means of the perfect gas mixture model in the local equilibrium approximation, while taking into account the chemical reaction rates. At the same time, the transport processes of the impulse, mass, and heat are considered in the approximation of binary like or unlike interactions between the gas species. In addition, the transport coefficients (viscosity η , thermal conductivity λ , diffusion D , and thermal diffusion α) are calculated with the modern molecular theory of gases [2]. The intermolecular potentials (IP) are the backbone of this theory. This is why the calculations of the transport properties of the gas substances presented in CVD processes demand the creation of a database (DB) containing (a) IPs of like or unlike interactions between the main

species participating in CVD and (b) calculational procedures for defining the transport properties.

Our DB EPIDIF is oriented mainly to the modeling of DIFusion processes of silicon gas-phase EPItaxy. Additionally, the set of components permits users to calculate the transport properties of the products of organic fuel combustion.

Several packages of computational programs for CVD process calculations already exist. One of them was developed at SANDIA Laboratory [3]. CVD Simulation Software has been promoted by PHOENICS [4]. To our knowledge, both these packages produce evaluations of the properties. The advantage of the DB EPIDIF is that it allows the user to estimate the uncertainties of the results, which is important for sensitivity analysis.

2. THEORETICAL BACKGROUND

2.1. Intermolecular Potentials for Binary Interactions Between Molecules

2.1.1. Polar and Unpolar Molecules

Instead of the widely used spherically symmetric Lennard–Jones (LJ) (12–6) potential, we use a generalized LJ (m –6) potential with three independent variable parameters: the equilibrium distance R_e , the potential well depth ε , and the repulsive parameter m for atom and unpolar molecule interactions. It can be written

$$\frac{U(R, \mathbf{a})}{\varepsilon} = \frac{6}{m-6} x^m - \frac{m}{m-6} x^6 \quad (1)$$

where $x = R_e/R$, R is the distance between two interacting particles, and \mathbf{a} is the vector of the parameters. The choice of this class of potentials is motivated (a) by the specificity of CVD processes for semiconductors, which often take place in light gas carriers, such as H_2 or He, and (b) by the possible participation of heavy globular molecules in the processes such as $SiCl_4$, MoF_6 , and WF_6 . It is well known that $m = 8$ to 9 for molecular hydrogen, while for WF_6 it is >15 . This contradiction cannot be resolved in the framework of the LJ (12–6) IP. Moreover, under some defined conditions, intermediate products of reactions (such as $SiH_4 \rightarrow SiH_3$, SiH_2 , SiH) could appear in the gas space. These particles do not exist as stable substances under normal conditions. It can be expected that estimation of the IP parameters of these components could be made using some methods developed for LJ (12–6) potentials.

The fact that we have already defined IP is not enough for modeling CVD processes. To carry out the transport property calculations, one also needs sets of reduced collision integrals (CI) $\Omega^{(l,s)*}(T^*)$ for each type of potential. For LJ ($m-6$) we have approximated [5, 6] over a wide range of reduced temperatures $T^* = T/\varepsilon$, from 0.4 to 200, and $m=8$ to ∞ the best available tables [7, 8] for $\Omega^{(1,1)*}(T^*)$, $\Omega^{(1,2)*}(T^*)$, $\Omega^{(2,2)*}(T^*)$, and $\Omega^{(2,3)*}(T^*)$ by means of a parameterized expression $\omega^{(l,s)}(T^*, m, \mathbf{a})$. Simultaneous approximation of $\Omega^{(l,s)*}(T^*)$ and $\Omega^{(l,s+1)*}(T^*)$ insured internal self-consistency of the CI. The collision integrals for the Sutherland potential have been included for the sake of the correct approximation at $1/m \rightarrow 0$.

Usually between the initial substances of the CVD processes and/or in the reaction products, there are also polar molecules, such as SiHCl_3 , HCl , HF , and H_2O molecules with large dipole moments μ . The interactions between like and unlike polar molecules are defined by means of a generalized Stockmayer ($m-6-3$) potential with a spherically symmetric kernel, e.g., LJ ($m-6$), and for CI we have

$$\langle \Omega^{(l,s)*}(T^*) \rangle = \omega^{(l,s)*}(T^*)(\text{LJ}(m-6)) + A_1 \delta^2/T^* \quad (2)$$

where the reduced dipole moment is $\delta = \mu_1\mu_2(T)/(d^3\varepsilon)$. The parameters $A_1 = 0.19$ and $A_2 = 0.20$ are taken from the calculations made earlier for LJ (12-6) by Brokaw [9]). Equation (2) was used to calculate the CI averaged with respect to the orientation. It was assumed that for polar-nonpolar molecular interactions the corrections bound to the dipole-induced dipole terms of IP could be neglected.

2.1.2. Quasi-Spherically Symmetric (Globular) Molecules

In the consideration of interactions in pure gases and mixtures, one has to keep in mind that many of the molecules (particularly the large ones) have low normal vibrational frequencies (of the order of about 100 to 200 cm^{-1}). As a result, at temperatures of 300 to 400 K and higher, these molecules are vibrationally excited. Therefore, the effective interatomic distances in the molecules increase with the temperature, and this leads to a corresponding change in IP. At a given temperature the gas of such molecules is considered as a mixture of different vibrationally excited states and the ground state [10]. The interaction between each pair is described by a LJ ($m-6$) potential with a slightly different increasing equilibrium distance. To a first approximation, we have an isotropic potential with temperature-dependent parameters (ITDP) [11] for calculation of the properties of these gases.

A special procedure and computational codes have been developed to take this phenomenon into account in the DB. It consists of the following steps.

- Calculating the temperature dependence of the relative populations of the excited levels.
- Defining the ITDP parameters $R_e^{\text{eff}}(T) = f(T)$, $\varepsilon^{\text{eff}}(T)$, and m while minimizing the weighted sum of squared deviations between experimental and calculated properties data (for example, second virial and diffusion coefficients and viscosity η). Here $f(T)$ is a correction obtained by multiplying the fourth variable parameter of the IP, δ_1 (enlargement of the molecule excited from the ground state to the first level), and the averaged relative population at temperature T .

This approach has been successfully applied to pure tetrahedral [11–13] (CF_4 , SiF_4 , CCl_4) and octahedral [11, 14, 15] (SF_6 , UF_6 , WF_6 , MoF_6) gases, BF_3 [16], and some mixtures of them [12, 17].

Then tables of $\eta(T)$ were reapproximated in the range 300 to 1500 K using three-parameter IP LJ ($m-6$) (1). These parameters (m , ε , and R_e) are included in the DB EPIDIF.

A problem which arises when applying the procedure described above is the lack of measured thermophysical properties for molecules with low vibrational frequencies. Usually, such experiments are carried out in a narrow temperature range ($T < 1000$ K) and often with a low accuracy.

2.2. Thermophysical Properties

2.2.1. Diffusion Coefficients

In the DB EPIDIF, the binary diffusion coefficients of i, j components of the gas mixtures (at pressure $p = 1$ atm) are calculated at a given T .

- $[D_{ij}]_1$ in a first theory approximation [1].
- $[D_{ij}]_2 = [D_{ij}]_1 (1 + \Delta)$ in a second theory approximation taking into account the slight influence (about 2%) of the sort of constituents x . The correction $(1 + \Delta)$ is calculated by means of an approximation [18] which includes only CI $\Omega^{(1,1)*}$, $\Omega^{(1,2)*}$, and $\Omega^{(2,2)*}$, the ratio of molecular weights M_1/M_2 , and the mole fraction x of the heavy component. At x and $M_1/M_2 = 1$, D_{ij} is a self-diffusion coefficient.

2.2.2. Viscosity

For pure gases, $\eta(T)$ is calculated by well-known expressions [2] in the second theory approximation.

The viscosity of a gas mixture (the number of components $k < 11$) is calculated as a matrix product,

$$[\eta_{\text{mix}}(T, \mathbf{x})] = \mathbf{x}^{\text{tr}} \mathbf{H}^{-1} \mathbf{x} \quad (3)$$

where \mathbf{x} is the mole fraction column vector. The dimension of the matrix \mathbf{H} as well as of the inverse \mathbf{H}^{-1} is given in a first approximation and is equal to $k \times k$, though its h elements include the viscosity values $[\eta_{ii}]_2$, $[\eta_{ij}]_2$, and $[\eta_{jj}]_2$ in the Storvick–Mason approximation [19]. For example,

$$[h_{ij}]_{\text{SM}} = -\frac{2x_i x_j}{[\eta_{ij}]_2} \frac{M_i M_j}{(M_i + M_j)^2} \left(\frac{5}{3A_{ij}^*} - 1 \right), \quad i \neq j. \quad (3a)$$

Here we have to keep in mind that the mixture viscosity derivatives over the potential parameter a_p required for the calculation of the viscosity confidence level are determined as

$$\frac{\partial(\eta_{\text{mix}})}{\partial a_p} = -\mathbf{x}^{\text{tr}} \mathbf{H}^{-1} \mathbf{H}' \mathbf{H}^{-1} \mathbf{x} \quad (4)$$

where \mathbf{H}' is a matrix of the element derivatives dh/da_p [20].

2.2.3. Thermal Conductivity

The calculation of the thermal conductivity for pure molecular gases includes terms which are proportional to the so-called collision numbers $Z_{\text{col}}(T)$ [$Z_{\text{rot}}(T)$ or $Z_{\text{vib}}(T)$]. There is space reserved in the DB for such information, although it is often not available at present. This is particularly true for interactions between unlike particles. The possibility of replacing $Z_{\text{col}}(T)$ and $Z_{\text{rot}}(T)$ with corresponding combinations of the binary self-diffusion coefficients as suggested by Uribe [21] is discussed.

The calculation of the thermal conductivity of chemically reacting mixtures requires additional terms to take into account the heat effects of the reactions. These depend on a number of factors which are too specific to be considered in the scope of our DB.

3. DATABASE FEATURES

The algorithms and data for calculations described above shape the top of the “thermophysical iceberg.” Its “underwater” foundation includes publications reporting the input potential-dependent thermophysical properties data of gases and their mixtures; critical analysis of the experimental

data; procedures for defining potential parameters and their variance-covariance matrix (VC matrix); statistical analysis of the calculated data; and, finally, using the DB by means of PC, marketing, management, and establishing connections with the users.

3.1. Considered Objects

The data in the DB EPIDIF can be divided into two groups.

3.1.1. Completely Investigated Molecules

This group consists of pure gases with well-measured properties in the temperature range of interest, such as Ar, Hg vapors, N₂, O₂, H₂, and CO₂. For these gases Russian GSSSD tables for $\eta(T)$ [22] were used. These tables were reapproximated by means of a LJ ($m-6$) potential [Eq. (1)]. The corresponding potential parameters and the VC matrix are given in the DB. The accuracy of the data measured for these gases, in particular, for Ar and N₂, has reached an extremely high level (with an uncertainty from 0.3 to 0.4%) due to joint efforts by thermophysicists from different countries.

In this group we also include the data for steam as a typical example of polar molecular gases. A special procedure for processing these data by means of the Stockmayer potential has been introduced recently [23].

A special place in this first group is occupied by heavy globular molecules (for example, BF₃, CH₄, SiH₄, GeH₄, CF₄, SiF₄, GeF₄, SiCl₄, GeCl₄, SF₆, UF₆, WF₆, and MoF₆). These data can be analyzed and processed using the ITDP approach. For some of them, the IP and corresponding thermophysical property tables have been produced at the Bulgarian Institute of Electronics during the last several years [11–17]. For others the available data are not sufficient or do not exist.

3.1.2. Partially Investigated Molecules

We reserve space for molecules for which we are still not ready to supply data and/or to recommend the procedures for calculations. We continue studying them because they also have a substantial impact on CVD processes. Here belong, for example, polar chlorine and fluorine molecules, such as SiHCl₃; atomic components with interactions governed by some potential curves (H, C, N, O, Si); and radicals of methane (CH₃, CH₂, CH), silane (SiH₃, SiH₂, SiH), or germane (GeH₃, GeH₂, GeH). At present, research is under way to choose/create appropriate procedures to enable us to define the IP in all these cases.

3.2. Interactions in Mixtures of Unlike Molecules

Presently, for multi component ($k \geq 4$) mixtures, unlike binary interactions dominate. Usually, these are calculated by means of empirical mixture rules for different physical properties, potential parameters, or potentials.

In our DB there are two possibilities: to use (a) the individual potential parameters of unlike molecule interactions a_{ij} , or (b) the usual combining rules such as $\varepsilon_{ij} = \sqrt{\varepsilon_{ii}\varepsilon_{jj}}$. Recently, a special procedure for simultaneous fit of different properties data of pure gases and binary mixtures has been developed [20]. It permits us to obtain simultaneously σ_{ii} , ε_{ii} , m_{ii} , σ_{ij} , ε_{ij} , and m_{ij} ($i=1, j=2$) using the least-squares method (LSM) and to obtain their VC matrix. This approach is applied in the DB to eight binary mixtures: Ar-H₂, Ar-N₂, H₂O-CO, H₂O-CO₂, H₂O-N₂, H₂O-O₂, N₂-O₂, and N₂-CO₂. Experimental D_{12} , η_{11} , η_{22} , and η_{mix} data were used to define the LJ ($m-6$) potential parameters and the corresponding VC matrix. Similar procedures for the binary mixtures of noble and some technically important gases have been reported by Kestin et al. [18]. The shortcoming of these results is the lack of a VC matrix.

Some results for the experimental N₂, O₂, and N₂-O₂ data approximation by means of weighted LSM (number of points $n=203$; LSM sum $S=34.8$) are listed in Table I.

For pure gases and gas mixtures Mason, Kestin, and coauthors developed the corresponding-states principle. For example, in 1989 Bzhovski et al. [24] calculated the viscosity, diffusion coefficient, and second virial coefficient of a great number of binary mixtures of noble and polyatomic gases. The results were acceptable with the exception of the mixtures of SF₆ and CF₄. Later, the calculations were repeated by means of ITDP [25] for three mixtures, SF₆-CF₄, SF₆-CH₄, and CF₄-CH₄. Then the deviations between experimental and calculated second virial coefficient data were diminished by a factor of 2 to 3, and new potential parameters

Table I. Parameters a_{ij} , IP (1) and $\text{RMS}^a \pm s_{ij}$ for Three Pairs, N₂-N₂, N₂-O₂, and O₂-O₂^b

a_{ij}	N ₂ -N ₂	N ₂ -O ₂	O ₂ -O ₂
d_{ij} (Å)	3.645 ± 0.015	3.509 ± 0.033	3.425 ± 0.022
ε_{ij} (K)	98.28 ± 2.77	110.75 ± 6.80	115.35 ± 4.65
m_{ij}	11.59 ± 0.34	11.60 ± 0.80	11.55 ± 0.55

^a Root Mean Square.

^b If $m_{11} = m_{22} = m_{12} = 12$, then $S = 37.0$; if $a_{ij} = f(a_{11}, a_{22})$, then $S = 37.9$.

were determined. Similarly, thermophysical properties of mixtures of WF_6 , UF_6 , and MoF_6 were calculated. We hope that this procedure will be useful for other cases considered in the DB.

4. STRUCTURE OF THE DB AND USER INTERFACE

To build the DB we used Borland C++ Builder.

Information on the potential parameters is included in a three-dimensional matrix, $C(3k, 3k, 6)$, where k is the number of the components and six is the number of two-dimensional matrix layers. Now we have $k=40$.

Currently the DB EPIDIF consists of the following gases: Ar, AsH_3 , C, Cl_2 , CO, CO_2 , F_2 , $\text{Ga}(\text{CH}_3)_3$, GeBr_4 , GeCl_4 , GeCl_3F , GeH_4 , H, H_2 , H_2O , HCl, He, HF, Hg, N, N_2 , O, O_2 , SF_6 , Si, SiBr_4 , SiCl_4 , SiF_4 , SiH, SiHCl_3 , SiH_2 , SiH_3 , SiH_4 , Si_2H_2 , Si_2H_6 , Si_3H_8 , SiI_4 , and WF_6 .

DB has the following options.

- to select a pair of molecules and to calculate at a given temperature T and mole fraction x their D_{ii} and D_{ij} in first and second approximations and η_{11} , η_{22} , and η_{mix} , together with the uncertainty levels for all values;
- to input any $k < 11$ mixture components and to calculate at a given T all binary diffusion coefficients and viscosities of gas mixture and estimated uncertainties; and
- to check the input data and change it if necessary.

5. CONCLUSION

A database was designed to assist engineers and researchers in the fields of microelectronics, materials and combustion sciences, and other fields where transport properties of molecular gases are important. It is user-friendly and helps rapidly to obtain a reliable general picture of the processes of interactions.

We continue to upgrade and improve the DB. Our future tasks concern the properties and potentials of like and unlike particle interactions for pure polar molecules and radicals and their mixtures with previously investigated molecules.

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