

Thermodynamics Modeling of Gas Phase Processes in Polycrystalline Diamond Deposition During Thermal Plasma Chemical Vapor Deposition

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Abstract

Polycrystalline diamond coatings are of great interests in engineering applications such as cutting tools as well as in biomedical applications. Such coating tools can be made by thermal plasma processes with high hydrogen dilution, where ion bombardment processes determines the film properties. In order to understand the physics behind the phenomena taking place during the deposition in the plasma medium we can divide the processes into gas phase and gas-surface reactions. In this work, gas phase thermodynamics equilibrium calculation for a thermal plasma reactor involving CH₄-H₂-Ar mixture was performed. Using the Gibbs free energy minimization method, the equilibrium composition of gaseous plasma phase species were calculated. The modeling of the plasma gas phase considers ionic species in addition to radicals and neutral species which mostly have been neglected in most of literature calculations due to the lack of thermodynamics data of ionic species. Our extensive results are obtained under the assumption that, at a particular temperature and pressure, equilibrium is achieved for all species considered in our model just before any solid carbon is allowed to be deposited. The presented model quantitatively predicts the molar concentration of plasma activated species. Our simulation results of equilibrium molar concentration of plasma species at different temperatures confirm the existing experimental observation in literatures. In addition, the initial, final and the change of the entropy, enthalpy, Gibbs and internal energies of the plasma reactor were evaluated at different temperatures.

Keywords: chemical vapor deposition, thermal plasma processes, plasma gas phase, Gibbs free energy

1. Introduction

Diamond films due to their extreme properties such as high hardness, high thermal conductivity, low coefficient of friction, relative good wear, temperature and corrosion resistant, good adhesion and adjustable tribological properties [1-4], as well as bio-compatibility and chemically inertness [2, 5] features are the best choice for many engineering and medical applications. However, the high cost of diamond films limits the commercial use to a few very specialized applications [6]. For these purpose, there have been too many researches on the CVD diamond production. These studies are done both on experimental optimization and also on theoretical modeling and simulation of this technology for understanding the fundamental phenomena during the deposition process [6]. Such basic researches

and model-based reactor designs leads to optimization and cost reduction of diamond film production.

Among usual methods for production of diamond films, chemical vapor deposition "CVD" is used extensively for a number of commercial applications [7-9]. However, plasma enhanced CVD "PE-CVD" method shows better operation conditions [10]. Plasma environment compared to the other deposition methods has the advantage of deposition at lower temperature of substrate along with higher growth rate, correspondingly. In PE-CVD methods poly-crystalline diamond films with good quality can be deposited, through decomposition of hydrocarbon gases such as CH₄, C₂H₂ and C₆H₆ mixed with H₂ and some noble gases like Ar in a DC, RF or microwave discharge [11-12]. However, the physics and chemistry of PE-CVD processes are not fully understood due to their complicated plasma-chemistry phenomena occurring inside the gas-phase and at the surface.

By separating the physico chemical phenomena into gas phase and gas-surface reactions, in this work, using a thermodynamic modeling, the equilibrium molar concentration of the plasma gas phase species in diamond film deposition of a CH₄-H₂-Ar system in a thermal plasma CVD will be calculated. The main purpose of this work and the new result is the thermodynamic modeling of the plasma gas phase. Moreover, in this model ionic species are included in addition to radicals and neutral species which mostly have been neglected in literature calculations due to the lack of their thermodynamic data. Our extensive results were obtained under the assumption that, at a particular temperature and pressure, equilibrium was achieved for all the species considered in our model under the limitation that no solid carbon was allowed to be deposited. The calculated results of molar concentration of the plasma gas phase species show good agreement with the literature experimental observations. Finally the entropy, enthalpy, Gibbs free energy and internal energy of plasma reactor will be calculated.

2. Nature of the Gas Phase in Thermal Plasma CVD

The nature of plasma chemical reactions in the gas phase and their interactions with the surface during the PE-CVD determines the properties of coats in engineering or medical applications. Thus one needs to investigate microscopically the plasma gas phase species and their molar concentration along with related reactions in order to understand the nature of these phenomena. For analytic investigation in our model we choose the ternary CH₄-H₂-Ar gas mixture as a common working gas mixture in PE-CVD of polycrystalline diamond films. In such mixtures CH₄ provides the carbon source and noble gases like Ar help the ionization of working gas, modify the surface morphology, and increase the

growth rate [14]. In addition, H₂ gas as a source of atomic hydrogen H and ionic form “H⁺” plays an essential role in production of activated radicals and ions from CH₄ and other hydrocarbons [15-16]. H₂ also destructs the polymeric carbon chain at the surface and etches the undesired species from the surface [15-16]. Here, we investigate some microscopic properties of the plasma medium such as species concentration, enthalpy, entropy, and Gibbs energies of different neutral and produced charged species just before any surface reactions occur.

A thermal plasma system is composed of high temperature gas particles. When a gas reaches high temperatures, the kinetic energies of neutral atoms and molecules are high enough to cause ionizations by collisions. Such collisional processes result in the ionization by thermal movement of particles. These ionization processes are observed in arc plasmas or burning flames when the gas temperature exceeds several thousand degrees [13]. Such conditions can be considered to be nearby thermal equilibrium [13].

In the plasma generated by a arc discharges, the energy distribution of the electrons (T_e) and the gas molecules (T_g) are almost the same, because the collision frequency between electrons and gas molecules become large.

Consequently, plasma will be at thermal equilibrium ($T_e \approx T_g$) [13]. When plasma is in thermal equilibrium, the density of particles can be calculated as a function of temperature and pressure [13]. As a general requirement for equilibrium, one can postulate that a system is in thermodynamic equilibrium when at constant temperature and pressure the total Gibbs energy of the system would be in minimum. In the case of a system undergoing chemical reactions, the Gibbs function is the significant property for defining the criteria of equilibrium. Such thermodynamic modeling and restrictions are thought to properly describe a situation in many shock tubes and discharge experiments during the intermediate stage of reactions [13].

3. Model Description for Computation of Equilibrium

Composition in Thermal Plasma

In the case of CH₄-H₂-Ar gas mixture, the equilibrium molar concentrations of the plasma gas phase species have been calculated using the Gibbs free energy minimization method. In all calculations temperature and pressure was kept constant. Also these calculations are independent of reactor volume. For such an investigation first we need to know all the possible species which could be formed in the plasma gas phase during the reactions. The species involved in the thermal plasma CVD of diamond were selected according to the experiments reported in [17] in which mass-spectroscopy measurements were carried out for a CH₄-H₂-

Ar microwave thermal plasma reactor. Thus, in our investigation in the plasma gas phase state of CH₄-H₂-Ar mixture we defined and categorized the most important species as follows:

- i. there is no negatively charged particle except electron: e⁻
- ii. formed or remaining non hydrocarbon neutral species: H₂, H, Ar
- iii. C₂ as the highest possible hydrocarbon is formed in our working temperature range which lead to hydrocarbons: C, CH, CH₂, CH₃, CH₄, C₂, C₂H, C₂H₂, C₂H₃, C₂H₄, C₂H₅, C₂H₆
- iv. only first time ionized species have been considered: Ar⁺, H⁺, H₂⁺, C⁺, CH⁺, CH₂⁺, CH₃⁺, C₂⁺, C₂H⁺, C₂H₂⁺, C₂H₃⁺, C₂H₄⁺, C₂H₅⁺ (except CH₄⁺ and C₂H₆⁺ which their thermodynamic data are not available)

In our study the total Gibbs energy of the system has been evaluated as the sum of all species partial molar Gibbs energy regarding their molar weight in the gas mixture as:

$$G_{\Sigma} = \sum_{N_g=1}^{N_g^t} G_{N_g} n_{N_g}, \quad (1)$$

where G_{Σ} is the total Gibbs energy function of the system in J, G_{N_g} is the partial Gibbs energy of N^{th} specie in J/mol, n_{N_g} is the number of the mole of N^{th} specie, and N_g^t is number of the total species in the gas phase of the plasma.

As long as the interaction between the species at equilibrium state is neglected, their mixture can be modeled as an ideal behaving gas mixture. Thus, the partial Gibbs energy of each particle in Eq. (1) can be written as:

$$G_{N_g} = G_{N_g}^{\circ}(T, P) + RT \ln(X_{N_g}), \quad N_g = 1, \dots, N_g^t, \quad (2)$$

where $G_{N_g}^{\circ}$ is the standard partial Gibbs energy of N^{th} specie in J/mol, R is universal gas constant in J.mol⁻¹.K⁻¹, X_{N_g} is the mole fraction of N^{th} specie, T is temperature in absolute scale, and P is pressure in atm.

The value of the standard partial Gibbs energy of gas specie ($G_{N_g}^{\circ}$) has been evaluated from the standard partial enthalpy and entropy of specie via Gibbsian relation ($G_{N_g}^{\circ} = H_{N_g}^{\circ} - TS_{N_g}^{\circ}$). In our constant pressure condition the temperature dependency of partial standard entropy, enthalpy and Gibbs energy (to be used in Eqs. (1, 2)) has been calculated using a simple polynomial form for heat capacity as:

$$\frac{C_{p,N_g}^{\circ}}{R} = \sum_{i=1}^I \alpha_{N_g,i} T^{(i-1)} = \alpha_{N_g,1} + \alpha_{N_g,2}T + \alpha_{N_g,3}T^2 + \alpha_{N_g,4}T^3 + \alpha_{N_g,5}T^4, \quad (3)$$

where $\alpha_{N_g,1}, \alpha_{N_g,2}, \alpha_{N_g,3}, \alpha_{N_g,4}, \alpha_{N_g,5}$ are the coefficients of the temperature dependence of the heat capacity function and C_{p,N_g}° is heat capacity in constant pressure in $\text{J. mol}^{-1} \cdot \text{K}^{-1}$.

For all neutrals (H_2 , Ar, CH, C_2H , ...) and simple charged species (e^- , H^+ , C^+ , Ar^+) the coefficients of the heat capacity function (see Eq. (3)) have been taken from [18], while for complex charged species (CH_2^+ , C_2^+ , C_2H_3^+ , ...) these parameters have been taken from [19].

Further on, the atomic population constrain of all basic elements (H, Ar, e and C) should be considered as:

$$p_j = \sum_{N_g=1}^{N_g^t} n_{j,N} n_{N_g}, \quad (4)$$

where $n_{j,N}$ is the number of the j -type atom in N^{th} specie (here j : H, Ar, e and C), p_j is the total population of the j -type atom in mol.

The mathematical equilibrium solution presented in the next section at a given temperature and pressure is the distribution of all n_{N_g} which minimizes the total Gibbs function of the system (see Eq. (1)) together with considering atomic population constrains (see Eq. (4)) along with a non negative n_{N_g} condition in the system.

4. Analytical Results of Equilibrium Composition in $\text{CH}_4\text{-H}_2\text{-Ar}$

System

A thermal plasma system can be generated with an arc discharge from low pressure of several Torr up to atmospheric pressure, although, it can be produced much more easily at relatively high pressure of more than hundreds Torr. In most PE-CVD experimental environments, the formation of polycrystalline diamond films takes place in the atmospheric or lower atmospheric pressure condition. Therefore, here for simulation of the total Gibbs minimization of the plasma gas phase the pressure has been kept at 50 Torr. In our evaluation based on experimental results in [20-21] the initial mole fraction of Ar, H_2 and CH_4 was considered to be 0.99, 0.008 and 0.002, respectively. The temperature zone for these simulations was varied from 298 till 5000 K. All computations have been performed using an in-house programming. The results of these calculations

present the equilibrium molar concentration of all possible species which exist at constant temperature and pressure in our thermal plasma reactor.

Figure 1 shows the calculated molar concentration of input gases (Ar, CH₄ and H₂) and the total electron concentration at different temperatures. As it can be seen only above 900 K there is enough energy for electron to appear and the rate of CH₄ decompositions increases around 1250 K.

Figure 2 represents the calculated equilibrium of final molar concentration of C₂, C₂H, CH, CH₂, CH₃ species as a function of the reactor temperature. According to these results the maximum molar concentration of CH₃ is achieved between 1300-3000 K, while the maximum concentration of C₂, C₂H, CH, CH₂ is achieved at 3925 K, 3300 K, 3500 K and 3175 K, respectively.

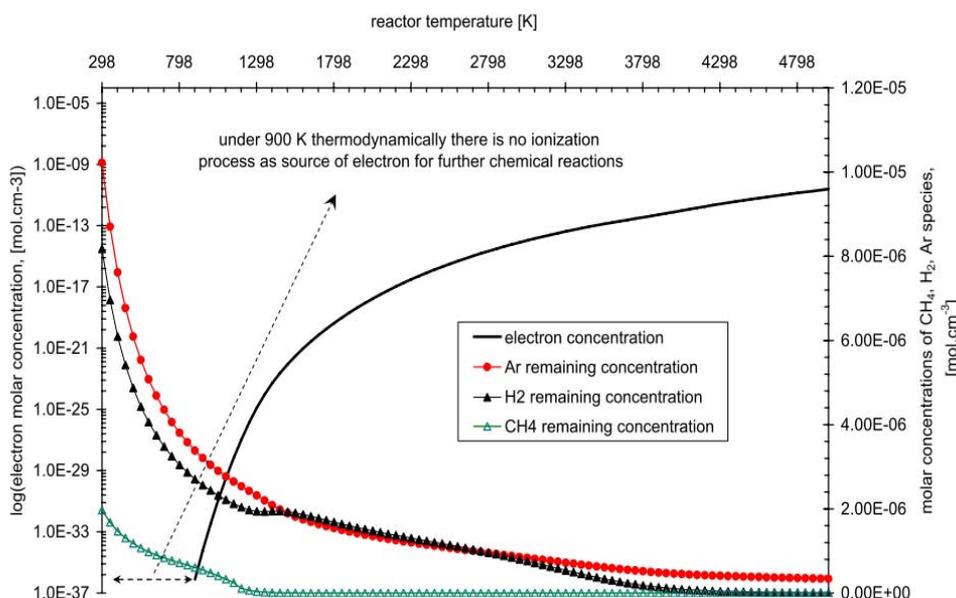


Fig 1. Calculated total remaining molar concentration of initial gases Ar, CH₄ and H₂ and the total produced electron as a function of reactor temperature.

Figure 3 represents the calculated equilibrium molar concentration of H, C₂H₂, Ar⁺, CH⁺, C₂H₅, C₂⁺, C₂H⁺, C₂H₂⁺, C₂H₃⁺ species. As it can be seen the maximum molar concentration of C₂H₂ achieved at 1350 K with a wide range of maximum peak varies from 1050 K to 3350 K. The maximum concentration of C₂H₅ is achieved at about 1200 K while the maximum concentration of H is at 4050 K. For some positively charged particles like Ar⁺, CH⁺, C₂⁺ the maximum concentration can be achieved only above 5000 K. Other ionic species like C₂H⁺, C₂H₂⁺, C₂H₃⁺ have their maximum concentration at 3600 K, 3400 K and 3250 K, respectively.

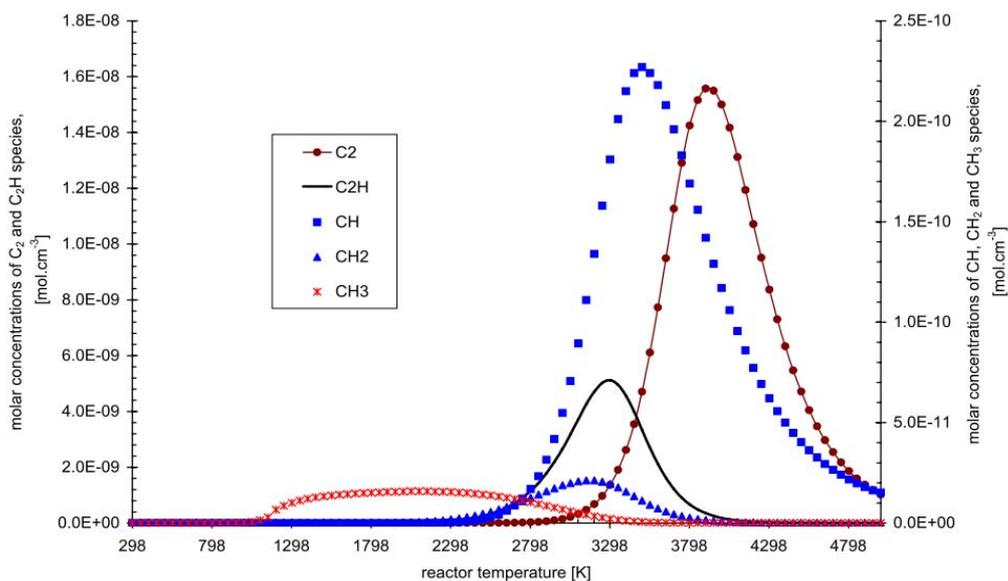


Fig 2. Calculated equilibrium molar concentration of the C_2 , C_2H , CH , CH_2 , CH_3 species as a function of reactor temperature.

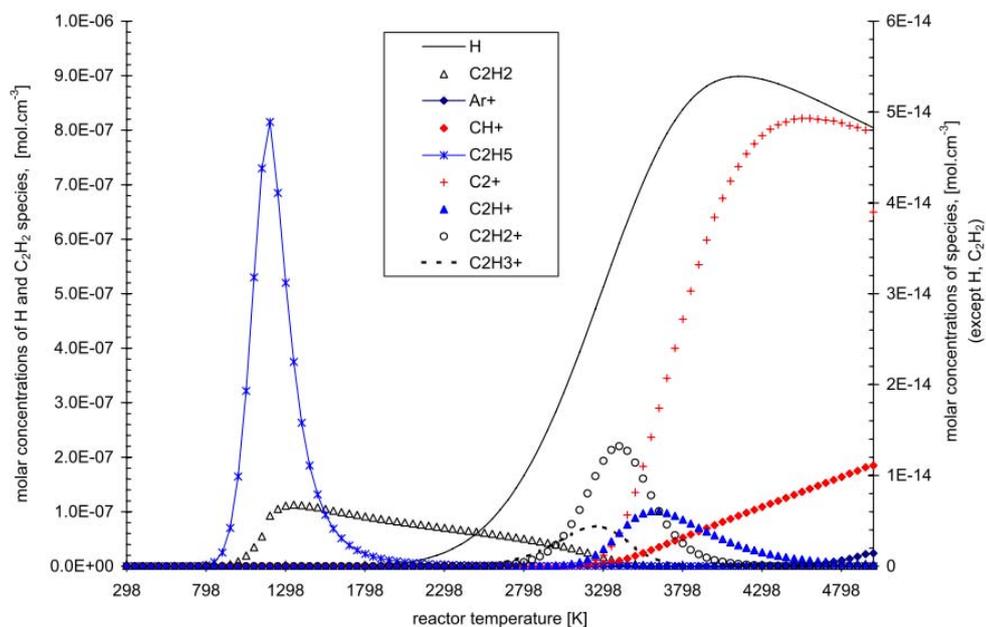


Fig 3. Calculated equilibrium molar concentration of the H , C_2H_2 , Ar^+ , CH^+ , C_2H_5 , C_2^+ , C_2H^+ , $C_2H_2^+$, $C_2H_3^+$ species as a function of reactor temperature.

Moreover, the calculated equilibrium molar concentration of H^+ , H_2^+ , C , C^+ , CH_2^+ , CH_3^+ , C_2H_3 , C_2H_4 , C_2H_6 , $C_2H_4^+$, $C_2H_5^+$ are presented in figure 4. As it can be seen the non ionic species like C_2H_6 , C_2H_4 , C_2H_3 achieve their maximum concentration at 1200 K, 1075 K and 2500 K, respectively, while for other ionic species H^+ , H_2^+ , C^+ , CH_2^+ , CH_3^+ , $C_2H_4^+$, $C_2H_5^+$ the maximum concentration appears above 3000 K.

5. Verification of Calculated Results

Regarding the deposition of polycrystalline diamond film in the CH_4 - H_2 -Ar system there exist some experimental data, determining the gas phase compositions, in literatures [20-21]. Rennick et al in [20] deposited thin polycrystalline diamond film using a 6.4 kW DC arc jet plasma, operating with CH_4 - H_2 -Ar gas mixtures. They used input flows of 1.8 SLM (standard liters per minutes) of H_2 , 60 SCCM (cubic centimeter per minute at STP) of CH_4 and an access of argon which made up a total flow of 13.2 SLM. They determined the absolute number density of H, CH and C_2 radicals using either cavity ring-down spectroscopy “CRDS” or diode laser absorption spectroscopy in [20]. Moreover Mankelevich et al in [21] used a DC arc jet reactor operating on CH_4 - H_2 -Ar gas mixture in thermal plasma chemical vapor deposition of nano and microcrystalline diamond deposition. Their model also presented the chemistry of the neutral and charge species [20].

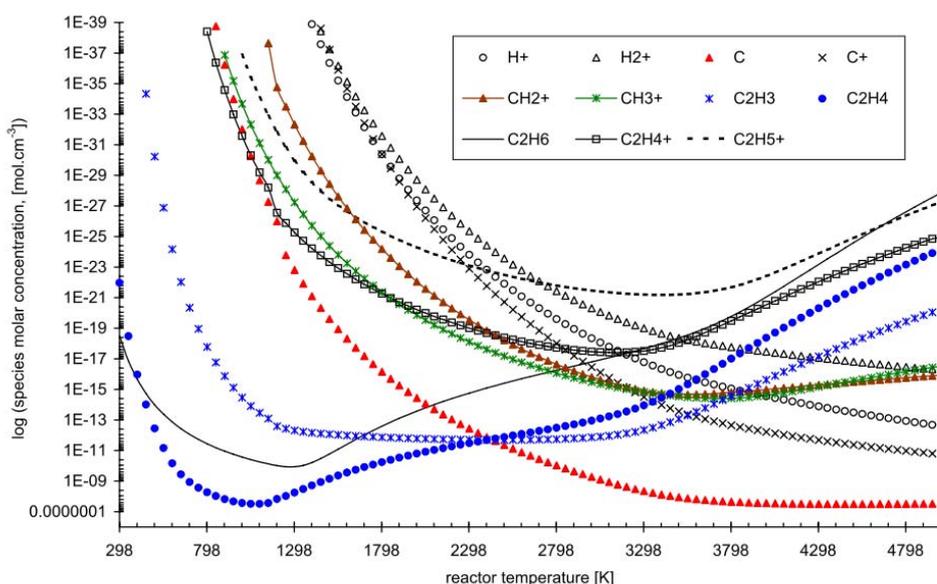


Fig 4. Calculated equilibrium molar concentration of H^+ , H_2^+ , C , C^+ , CH_2^+ , CH_3^+ , C_2H_3 , C_2H_4 , C_2H_6 , $C_2H_4^+$, $C_2H_5^+$ species as a function of reactor temperature.

Our calculated results of molar concentration of species (figures 2-4) show good agreement with experimental results in [20-21] and simulation in [21]. The calculated molar concentration of plasma species C_2 , CH and C_2H , CH_2 are presented along with the existing experimental data from [20-21] in figures 5.a and 5.b, respectively. Experimental verification of calculated molar concentration of the species CH^+ , Ar^+ and H, C_2H_2 are represented in figure 6.a and figure 6.b, respectively. Furthermore, Figures 7.a and 7.b show the calculated molar concentration of species H^+ , C^+ , CH_3^+ and C, C_2H_4 , respectively along with the existing experimental data.

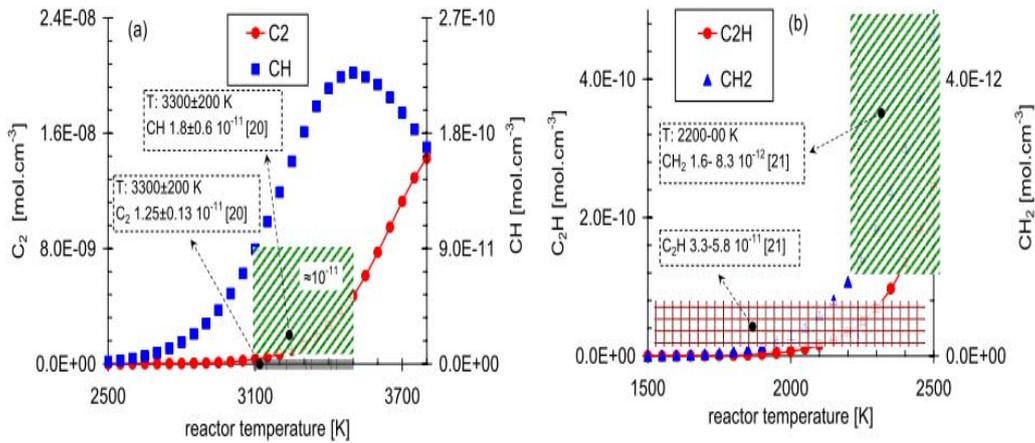


Fig 5. Verification of the calculated molar concentration of plasma species with existing experimental data as a function of reactor temperature; a: C_2 , CH and b: C_2H , CH_2 .

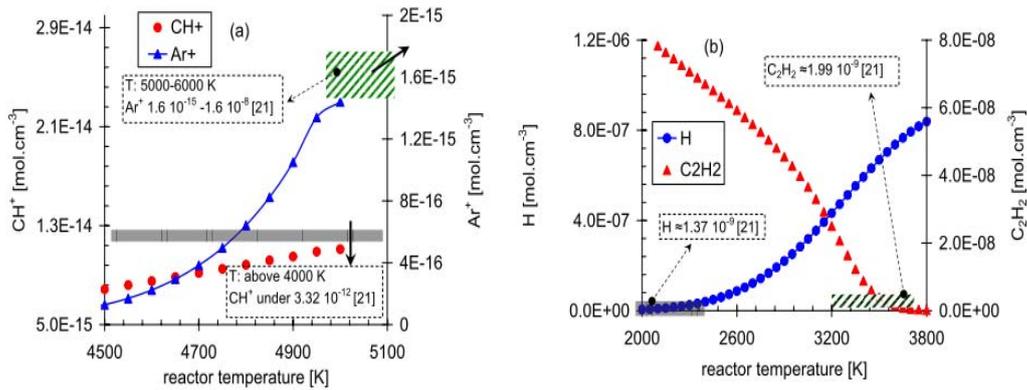


Fig 6. Verification of the calculated molar concentration of plasma species with existing experimental data as a function of reactor temperature; a: CH^+ , Ar^+ and b: H, C_2H_2

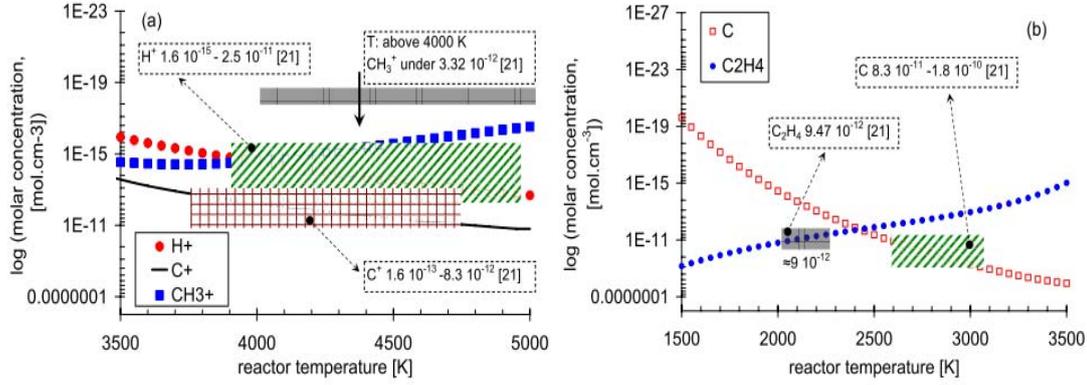


Fig 7. Verification of the calculated molar concentration of plasma species with existing experimental data as a function of reactor temperature; a: H⁺, C⁺, CH₃⁺ and b: C, C₂H₄.

6. Calculation of Enthalpy, Entropy, Gibbs and Internal Energy of Reactor

Fundamental thermodynamics properties like entropy, enthalpy and Gibbs energy helps us to find the equilibrium state of the system at each temperature, pressure and volume. For this calculation we need to consider all formed species in the plasma medium and the reactions which occur between these species. Here, in order to evaluate the change of the entropy, enthalpy, Gibbs and internal energies of the system we need to calculate the initial and final (equilibrium) state of the system. The initial state of the system is only attributed to the initial inlet gas mixture (CH₄, Ar and H₂). However, the final state is described by all species produced in the plasma gas phase (figures 2-4). The enthalpy and entropy of all species have been evaluated using

$$\frac{H_{N_g}^{\circ}}{RT} = \sum_{i=1}^I \frac{\alpha_{N_g,i} T^{(i-1)}}{i} + \frac{\alpha_{N_g,I+1}}{T} = \alpha_{N_g,1} + \frac{\alpha_{N_g,2}}{2} T + \frac{\alpha_{N_g,3}}{3} T^2 + \frac{\alpha_{N_g,4}}{4} T^3 + \frac{\alpha_{N_g,5}}{5} T^4 + \frac{\alpha_{N_g,6}}{T}, \quad (5)$$

And

$$\frac{S_{N_g}^\circ}{R} = \alpha_{N_g,1} \ln(T) + \sum_{i=2}^I \frac{\alpha_{N_g,i} T^{(i-1)}}{(i-1)} + \alpha_{N_g,I+2} = \alpha_{N_g,1} \ln(T) + \alpha_{N_g,2} T + \frac{\alpha_{N_g,3}}{2} T^2 + \frac{\alpha_{N_g,4}}{3} T^3 + \frac{\alpha_{N_g,5}}{4} T^4 + \alpha_{N_g,7}, \quad (6)$$

while their temperature dependency follows from their interrelation with C_{p,N_g}° function represented by Eq. (3). Figure 8 shows the change of the total enthalpy and entropy of the system as a function of the reactor temperature. As it can be seen there is a little change in the total enthalpy and entropy of the system up to 1250 K where CH_4 starts to decompose. Furthermore, in the range of 1250–3200 K a slow increase can be found and at temperatures above 3200 K entropy and enthalpy increases rapidly.

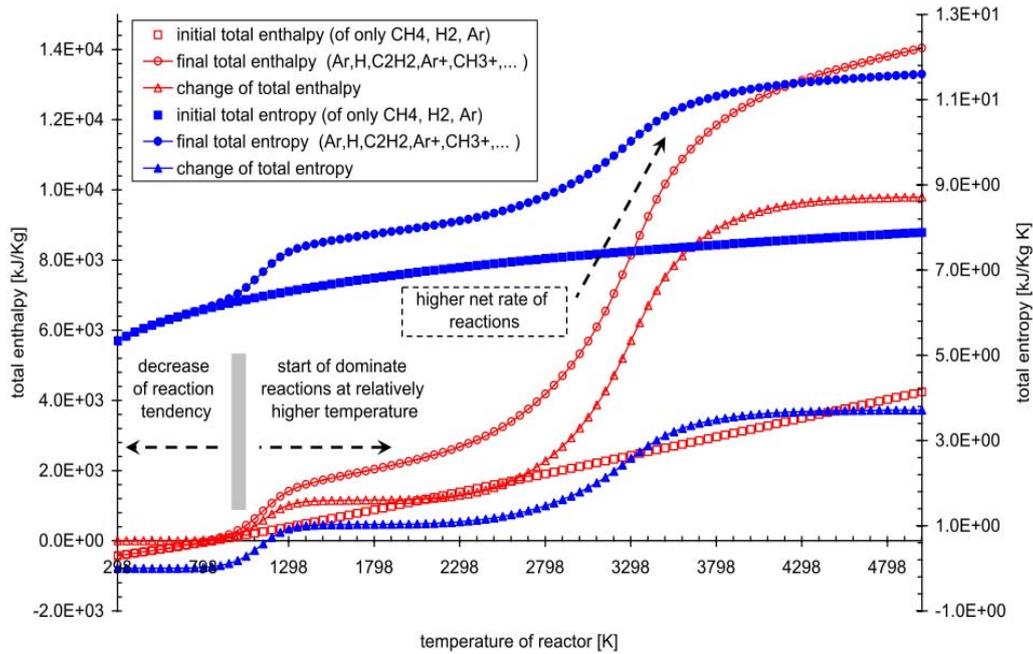


Fig 8. Calculated initial, final (equilibrium), and change of the total enthalpy and entropy of the system as a function of reactor temperature.

The internal energy $U_{N_g}^\circ$ can be found from the specific heat capacity at constant volume C_{v,N_g}° for an ideal gas system ($C_{v,N_g}^\circ = C_{p,N_g}^\circ - R$) in each reactor temperature by $U_{N_g}^\circ = H_{N_g}^\circ - RT$. Figure 6 shows the initial, final, and changes in the Gibbs and internal energies of the system (considering all species) as a function of temperature. According to these results the change of Gibbs energy of

the system shows a negative slope representing the higher tendency of all chemical phenomena to occur at higher temperatures. This means that these reactions spontaneously occur. In addition since the enthalpy is the dominant term in the internal energy function, the temperature dependency of the internal energy of the system in figure 9 shows similar slope behavior as that of the enthalpy curve in figure 8.

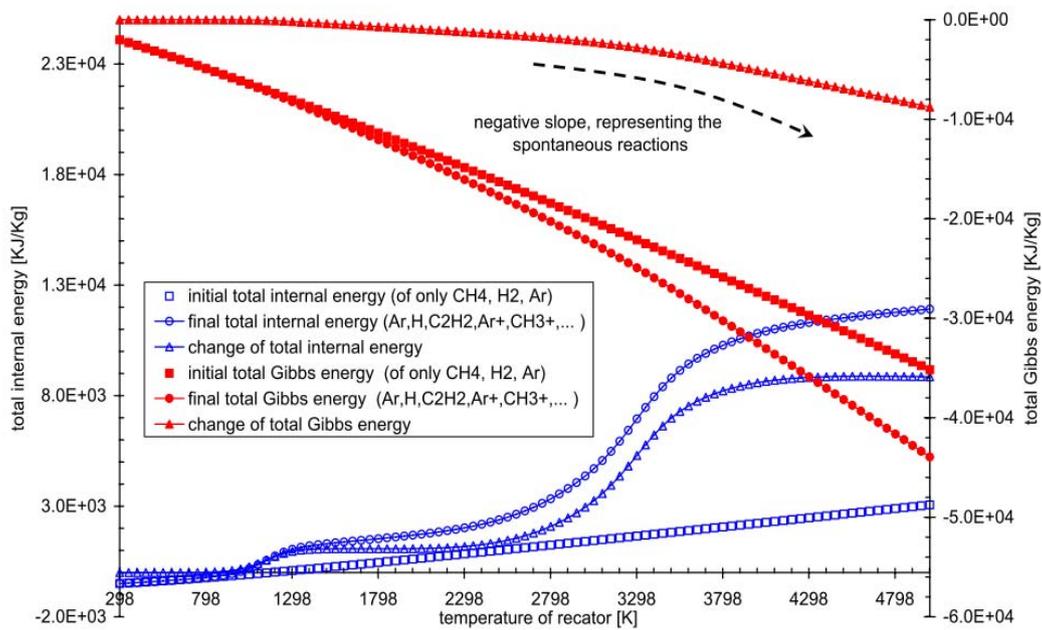


Fig 9. Calculated initial, final and changes in the Gibbs and internal energies of the system as a function of temperature.

7. Conclusions

A thermodynamic modeling for the gas phase plasma for polycrystalline diamond deposition during thermal plasma CVD has been studied theoretically. In this work the ternary CH₄-H₂-Ar gas mixture has been considered regarding all formed species in plasma and their interaction with surface species along with neglecting the surface process. In this investigation the C₂ hydrocarbons were considered as the maximum number of carbon combinations. Then, using the Gibbs energy minimization method the equilibrium molar concentrations of all

species formed in the plasma medium were calculated. The results of the model confirm the existing literature values. Moreover, the initial, final and change of entropy, enthalpy, internal energy, and Gibbs free energy of the plasma gas phase as a function of reactor temperature have been calculated and presented.

The results of the equilibrium molar concentrations of all possible gas phase species which could exist at a given temperature are the essential information needed to model, simulate and understand the gas-surface processes during the deposition phenomena. These results show macroscopic behaviors of the plasma gas phase at different temperatures. Such thermodynamic modeling and restrictions are thought to properly describe a situation in many shock tubes and discharge experiments during the intermediate stage of reactions.

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Received: September, 2011