Chemisorption of hydrocarbon species on transition metals during diamond chemical vapor deposition

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Abstract

This paper presents a brief discussion of the phenomena associated with chemisorption of hydrocarbon species on transition metals during diamond chemical vapor deposition. The concepts relevant to the surface energetics are summarized, and the methods developed for the calculation of surface chemisorption energies are reviewed. Chemisorption energies of methyl radicals on transition metals are estimated on the basis of published results. The estimated chemisorption energies of CH_3 on Ni, Co, Fe, W (Mo), Ta and Ti are 36, 34, 43, 64, 85 and 85 kcal/mole, respectively. The results provide the necessary input parameters for studies of diamond nucleation kinetics.

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Introduction

Recent experimental studies on the nucleation and early stages of growth have led to significant strides in the understanding of mechanisms governing diamond nucleation during chemical vapor deposition (CVD) [1]. A number of nucleation enhancement methods and oriented nucleation methods have been developed that enable control of diamond nucleation density over several orders of magnitude and allow heteroepitaxial, highly oriented growth of diamond on Si, Ni, Ti, or Co [2–6]. The importance of gas/substrate interactions and surface adsorption states in the early stage of diamond nucleation has been identified [7–9] and the effects of surface pretreatment methods and process parameters on surface states have been investigated in connection with diamond nucleation [2–6,9–13]. Theoretical studies on diamond nucleation kinetics [7,14] have also attracted an increasing attention.

It has been frequently observed that an incubation, or nucleation delay period exists in diamond CVD processes. This incubation period may be related to the gas/surface interactions [7,8]. The adsorption and diffusion of gas phase species on the surface critically influence the incubation period and cluster formation, and hence the nucleation kinetics of diamond [7]. In order to quantitatively study the nucleation kinetics of diamond during CVD and to ascertain the mechanisms of nucleation enhancement and oriented nucleation of diamond, knowledge of surface adsorption energetics of growth species for diamond is needed. However, no quantitative experimental measurements or theoretical calculations have been reported for the surface adsorption energetics in the initial nucleation stage of diamond CVD. Therefore, the objective of the present work is to determine the surface adsorption energies of a hydrocarbon species (CH_3) on transition metal substrates (Mo, W, Ta, Ti, Ni, Co, and Fe) during diamond CVD. The selection of CH_3 and the transition metals is prompted by the fact that CH_3 is one of the dominant growth species for diamond [15], and Mo, W and Ta have been widely used as substrates for diamond deposition [1], while Ti, Ni and Co have been examined as substrates for diamond heteroepitaxy [2]. Although Fe is not a common substrate material, it is also considered in this study due to its use as a thin overlayer in substrate coating pretreatment [16] and in steels [17].

In this paper, the phenomena associated with surface adsorption are discussed briefly. This is followed by a description of the concepts and definitions relevant to surface energetics, and a review of the empirical and theoretical methods developed for the calculation of chemisorption energies. Due to a lack of appropriate methods for the present problem, the chemisorption energies of CH_3 on the transition metal substrates are estimated by analogy with those of C_2H_4. In view of the high substrate temperatures employed in common diamond CVD processes [1], the emphasis of this study is placed on chemisorption processes.

Surface adsorption and energetics

Depending on the nature of gas/surface interactions, one usually distinguishes between two broad classes of adsorption processes, physisorption and chemisorption. In physisorption, the interaction between an adsorbed molecule and the surface is relatively weak, and the attractive force is van der Waals and/or electrostatic. Chemisorption involves a more intimate interaction, where an adsorbed molecule may break up into its component atoms or smaller fragments, which are chemically bound to the surface. One of the important physical properties that characterize the gas/surface interactions is the energy of the surface bond, E_{bond}, or, adsorption energy, E_a. In physisorption, the adsorption energy is typically lower than 10 kcal/mole. In chemisorption, the adsorption energy may range from 20 to 200 kcal/mole, depending on the nature of surface-adsorbate and whether molecules dissociate during adsorption.

The adsorption energy of a gas on a surface is usually determined indirectly by measuring the heat of adsorption (or the heat of desorption) of the gas, ΔH_{ads}, which is always positive. To define the adsorption energy, consider the chemisorption of a diatomic molecule, X_2, onto a site, M, on a uniform solid surface, where M represents the adsorption site at which bonding occurs to a cluster of atoms or to a single atom. If the molecule adsorbs without dissociation (molecular adsorption case), the adsorption energy is defined as the energy needed to break the MX_2 surface chemical bond:

$$E_a = \Delta H_{ads} = E_{bond}(\mathrm{MX_2}),$$

where ΔH_{ads} is defined as: $\mathrm{MX_2}(ads) \xrightarrow{\Delta H_{ads}} \mathrm{M} + \mathrm{X_2}(gas)$.

However, if the diatomic molecule dissociates during adsorption (atomic adsorption case), the adsorption energy is defined as a difference of the energy needed to break two MX surface chemical bonds and the dissociation energy of the X_2 gas molecule, E_{diss}:

$$E_a = \Delta H_{ads} = 2E_{bond}(\mathrm{MX}) - E_{diss},$$

where ΔH_{ads} is defined as: $2\mathrm{MX}(ads) \xrightarrow{\Delta H_{ads}} 2\mathrm{M} + \mathrm{X_2}(gas)$.

For polycrystalline metals, there is a large variation in the heat of chemisorption resulting from multiple binding sites for a given crystal plane or from crystal face to crystal face. In general, there is not a single-valued heat of chemisorption for a given metal-adsorbate system. However, one can obtain an averaged chemisorption energy over polycrystalline surfaces of a metal.

Approaches to chemisorption energetics

Both empirical and theoretical approaches have been developed for the prediction of chemisorption energies.

Early empirical methods determining chemisorption energies essentially ignore the surface structure and frequently presume that an adsorbing atom reacts with a single surface atom. Eley [18] adapted Pauling's [19] approximation to the adsorption of hydrogen atoms on metals, where the metal-hydrogen bond strength was taken as the arithmetic or geometric average of the metal-metal and the hydrogen molecule bond strengths. Similar approximations have been made for other gas molecules on metals [20], but the agreement of the calculated results with experiments is poor. The approximation of the chemisorption energies of C on metals using metal-carbon bond energies in the corresponding bulk carbides also appears to be questionable for certain metals, as demonstrated by the large difference between the computed Ni-C covalent bond strength (55 kcal/mole) in NiC and the experimentally measured chemisorption energy (170 kcal/mole) for C on Ni (100) surface [21]. In another empirical method [22], the heat of chemisorption is approximated by the heat of formation of the corresponding bulk compound. However, the correlation of the chemisorption energies of C on transition metals to the heats of formation of the corresponding carbides is rather poor and does not seem to be useful for predictive purpose [22].

Theoretical methods that provide valuable insight into the electronic structures of adsorbates on surfaces include *ab initio* quantum chemical methods [23], full-potential linearized augmented plane wave (FLAPW) method [24], X_α method [25], effective medium approach [26], crystal orbital-type methods [27], and cluster model [28]. Among these, the cluster model, coupled with *ab initio* quantum chemical methods or local density and semi-empirical methods, has been frequently used to treat chemisorption phenomena on transition metal surfaces. It has been shown [29] that qualitatively reasonable results can be obtained if transition metal atoms are treated as one-electron systems using Effective Core Potentials (ECP). However, apart from the accuracy of the one-electron ECP approximation, it still remains unclear in cluster modeling how many atoms are required to reproduce actual metal surface conditions. Generally, it is taken for granted that the Fermi level and/or the continuous density of states have to be well reproduced by a cluster if a surface model is to be considered reasonable [27]. However, a quantitative reproduction of the Fermi level requires very large clusters. An error in the chemisorption energy, at least 10 kcal/mole, is expected even for a 300–400 atom cluster [30]. In addition, the chemisorption energies calculated using the cluster model oscillate strongly with cluster size. Attempts to remedy the poor cluster convergence with embedding methods have been moderately successful [31]. Therefore, the cluster model produces results for the chemisorption energies only of a qualitative nature, rather than a quantitative nature.

Estimation of chemisorption energies of CH_3 on transition metals

Experimental measurements of the heats of chemisorption of CH_3 on transition metals are very difficult because of the high reactivity of CH_3. Only the heats of chemisorption on Ni [32,33] and Pt [34] have been calculated using the cluster model and reported in literature. Therefore, empirical or theoretical approaches must be used for the estimation of chemisorption energies of CH_3. In view of the inadequacy of the existing empirical and theoretical methods for the present problem, as discussed above, alternative methods must be developed.

Inspection of relevant literature [20,35] shows that the average values of the chemisorption energies of C_2H_4, CO, CO_2, N_2, H_2 and NH_3 on transition metals all follow a common pattern, i.e., the values decrease from left to right across the Periodic Table for the different adsorbate-metal systems: Ti(Ta)>Nb>W(Cr)>Mo>Fe>Mn>Ni(Co)>Rh>Pt(Pd)>Cu(Au), as illustrated in Figure 1 for C_2H_4. This correlation between the heats of chemisorption and the position of metals in the Periodic Table suggests that some specific property of the metals, rather than adsorbing gases, determines the relative activity of the metals in chemisorption and hence the trend of variation in chemisorption energies [20]. Therefore, it is reasonable to assume that the heats of chemisorption of CH_3 on transition metals also follow the same trend.

CH_3 and C_2H_4 are both sp^2 hybridized and exhibit the same orbital character [36], which determines the trend of variation in heats of chemisorption [20]. The strengths of the C-H bonds in C_2H_4 and CH_3 are comparable due to the sp^2 hybridization. In addition, the chemisorption of C_2H_4 on Ni films or on W involves the breakage of C-H rather than C-C bonds [20]. Therefore, it is proposed in this study that the chemisorption energies of CH_3 on the transition metals may be estimated from the trend for C_2H_4 outlined in literature (Figure 1). The proposed methods are described as follows:

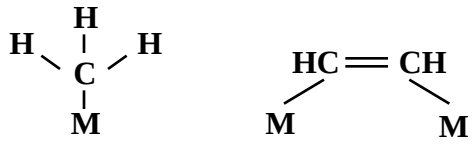
(a) From the value of chemisorption energy of CH_3 on Pt [34], the chemisorption energy of CH_3 on a given transition metal, $\left(\Delta H_{CH_3}\right)_{Metal}$, is extrapolated using the relationship

$$\left(\Delta H_{CH_3}\right)_{Metal} \Big/ \left(\Delta H_{CH_3}\right)_{Pt} = \left(\Delta H_{C_2H_4}\right)_{Metal} \Big/ \left(\Delta H_{C_2H_4}\right)_{Pt},$$

where Metal = Ti, Ta, W, Mo, or Fe. This extrapolation yields the data of the heats of chemisorption of CH_3 on the transition metals, as plotted in Figure 2. Cubic polynomials have been fit to the data in order to obtain interpolated values of chemisorption energies for other substrate materials (for example, Mn and Co).

(b) Alternatively, $\left(\Delta H_{CH_3}\right)_{Metal}$ may be calculated from the Metal-C bond energy in the corresponding Metal-C_2H_4 system based on the following arguments. By definition, $\left(\Delta H_{CH_3}\right)_{Metal}$ may be taken as equal to the Metal-C bond energy in the corresponding Metal-CH_3 system,

$\left(\Delta H_{CH_3}\right)_{Metal}$ = $\left(E_{M-C}\right)_{Metal\text{-}CH_3}$, since the chemisorption of CH_3 on metals takes place prior to its dissociation or H abstraction [25]. The chemisorption of C_2H_4 on metals, however, involves the breakage of C-H bond and H abstraction, and the conversion from C_2H_4 to C_2H_2 occurs on the metal surface under typical diamond CVD conditions [25]. The configurations of surface bonds in CH_3 and C_2H_4 chemisorption are schematically shown below:



Again, by definition, the chemisorption energy of C_2H_4 on a given transition metal, $\left(\Delta H_{C_2H_4}\right)_{Metal}$, may be expressed as

$$\left(\Delta H_{C_2H_4}\right)_{Metal} = 2\left(E_{M-C}\right)_{Metal\text{-}C_2H_2} - 2\left(E_{H-C}\right), \qquad (1)$$

where E_{H-C} is the energy required to break a H-C bond in a C_2H_4 adsorbed on the metal surface. Assuming that the Metal-C bond energy in a Metal-CH_3 system be equal to the Metal-C bond energy in a Metal-C_2H_2 system, $\left(E_{M-C}\right)_{Metal\text{-}CH_3}$ = $\left(E_{M-C}\right)_{Metal\text{-}C_2H_2}$, the chemisorption energy of CH_3 on the given transition metal may be then calculated using the formulation

$$\left(\Delta H_{CH_3}\right)_{Metal} = \left(E_{M-C}\right)_{Metal\text{-}CH_3} = \left(E_{M-C}\right)_{Metal\text{-}C_2H_2}. \qquad (2)$$

From the known chemisorption energies of C_2H_4 and CH_3 on Pt, E_{H-C} is calculated by combining Eqs. (1) and (2) to be 14 kcal/mole which is comparable to the results reported in literature [37,38]. Then, from the known chemisorption energies of C_2H_4 on the transition metals (Figure 1) and using Eqs. (1) and (2), the chemisorption energies of CH_3 on the respective metals can be calculated, as plotted in Figure 2. Clearly, the chemisorption energies estimated using the extrapolation and calculation methods exhibit good agreement, suggesting the validity of these approaches for the present problem. In addition, the estimated chemisorption energies appear to reasonably reflect the trend of the ease of diamond nucleation on the transition metals during CVD [7].

In summary, the calculated results provide the necessary input parameters for studies of diamond nucleation kinetics and form a useful starting point for exploring the mechanisms of nucleation enhancement and oriented nucleation of diamond. Further studies are under way to investigate the structure and size of the critical nucleus for diamond nucleation on transition metals during CVD.

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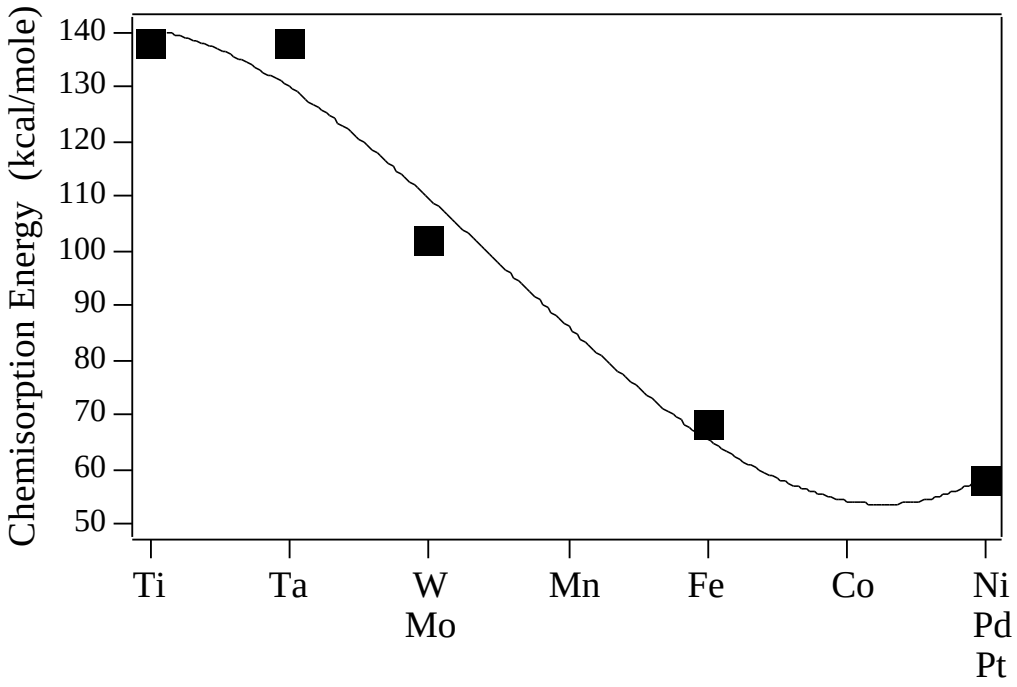

Figure 1. Chemisorption energies of C_2H_4 on transition metals. The data are obtained from Ref. [20] and the curve is fit to the data using cubic polynomials.

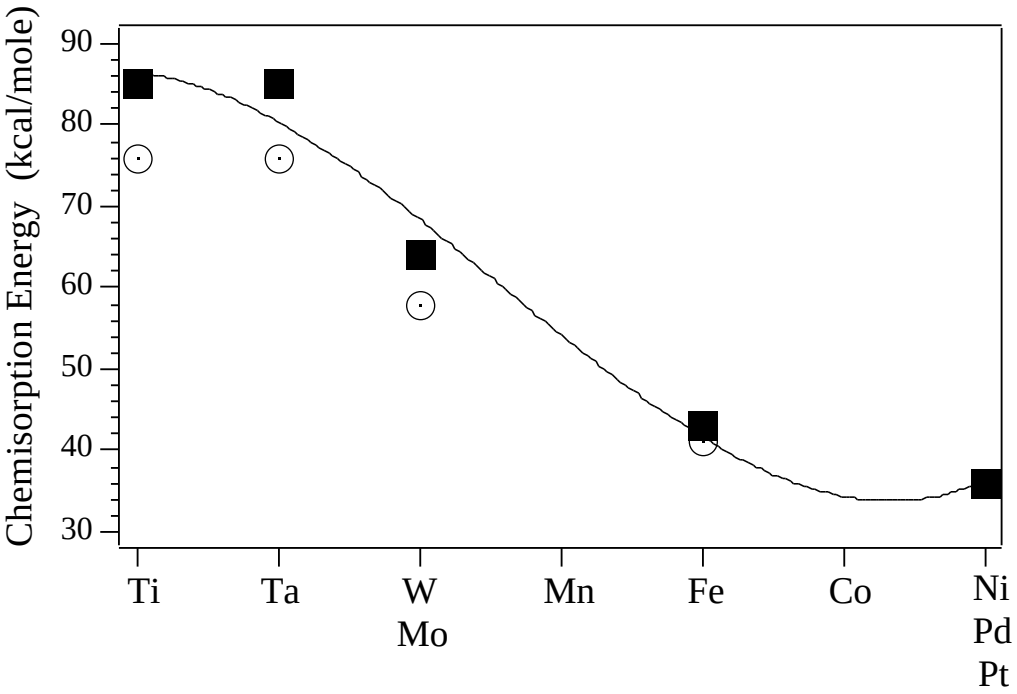

Figure 2. Chemisorption energies of CH_3 on transition metals. The data for Pt is obtained from Ref. [34]; the data for all other metals are extrapolated (squares) or calculated (open circles) using methods (a) or (b) proposed in this study; the solid line is fit to the extrapolated data using cubic polynomials.

Table 1. Heat of chemisorption of CH_3 in kcal/mol

Gas	Ti	Ta	W	Mo	Mn	Fe	Co	Ni(Pt,Pd)
ΔH_{CH_3} (a)	85	85	64	64	54	43	34	36[34-36]
ΔH_{CH_3} (b)	76	76	58	58	51	41	34.5	36