

# A Nanoscaled Thermodynamic Approach in Nucleation of CVD Diamond on Nondiamond Surfaces

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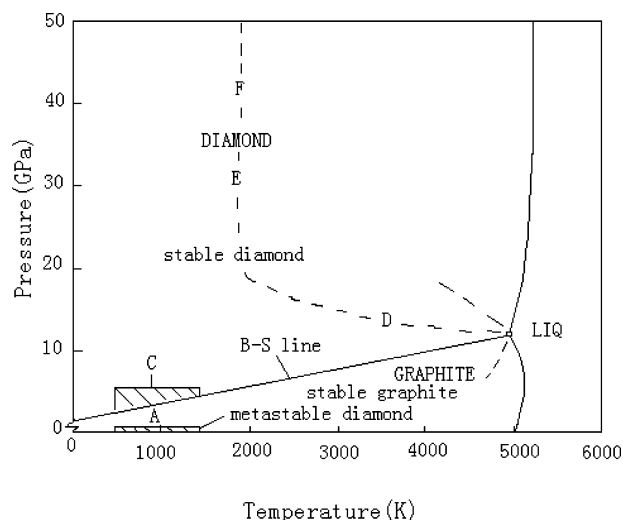
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Based on the carbon thermodynamic equilibrium phase diagram, a nanoscaled thermodynamic approach, taking the effect of nanosize-induced additional pressure on Gibbs free energy of diamond critical nuclei and phase transition probability from graphite to diamond into account, was performed to elucidate diamond nucleation on nondiamond surfaces upon chemical vapor deposition (CVD). The theoretical analysis showed that the capillary effect of the nanosize curvature of diamond critical nuclei could drive the metastable phase region of nucleation of CVD diamond into a new stable phase region in the carbon diagram. Consequently, diamond nucleation is preferable to graphite phase formation in competing growth of diamond and graphite upon CVD.

## I. Introduction

The quest for artificial methods to grow diamond thin films on nondiamond substrates has attracted great interest due to its enormous potential for technological applications.<sup>1</sup> Diamond films are typically grown as a thermodynamic metastable phase by the means of low-pressure CVD over the last 20 years.<sup>2</sup> Many significant advances were made in the intensive research and development in the past few years. For instance, very recently, high-quality heteroepitaxially growth of CVD diamond on iridium was reported.<sup>3–4</sup> Then, the growth of large-area single-crystalline diamond films on nondiamond surfaces still remains a great challenge for physicists and materials scientists.<sup>5</sup> For this issue, one of the major obstacles is that nucleation of CVD diamond remains much less understood and largely relies on trial and error.<sup>6</sup> For instance, the presence of atomic hydrogen etching graphite phase and helping  $sp^3$  hybridization of carbon atom has been considered essential.<sup>7</sup> However, some studies reported that diamond films were grown upon CVD with a hydrogen-free environment.<sup>8–9</sup> It is therefore essential to understand the basic chemical and physical process involved in nucleation of CVD diamond. CVD diamond is usually a typical quasi-equilibrium process, and pressure is in the range of  $10^2$  to  $10^5$  Pa and temperature is in the range of 1000–1300 K.<sup>2,10</sup> Thus, nucleation and growth region of CVD diamond can be marked as the **A** region in the carbon phase diagram shown in Figure 1.<sup>11</sup> Thermodynamically, the **A** region belongs to the metastable region of the diamond phase and the stable region of the graphite phase. Naturally, graphite nucleation would be prior to diamond nucleation in the **A** region from the point of view of thermodynamics. Therefore, diamond nucleation would not happen when graphite nucleation is restrained or stopped. Actually, this is an important physical foundation-stone of the presence of atomic hydrogen in CVD diamond due to its more etching rate to graphite phase and less etching rate to diamond phase. However, would CVD diamond nucleation really be in the metastable phase region in the carbon phase diagram upon



**Figure 1.** Carbon thermodynamic equilibrium phase diagram. The **A** region means a metastable phase region of CVD diamond nucleation; the **C** region means a new stable phase region of CVD diamond nucleation with respect to the effect of nanosize-induced additional pressure.

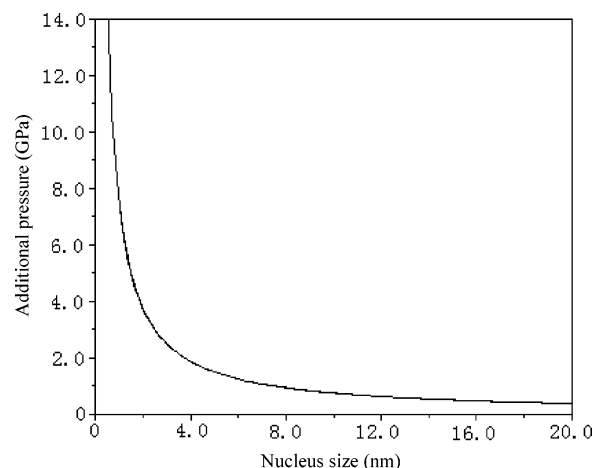
CVD? This issue should be treated discreetly. On the other hand, it has been substantiated, basically, that CVD diamond nucleation on nondiamond surfaces is a complex process of surface chemical reactions and physical nucleation, and the chemical process is the main factor causing CVD diamond nucleation.<sup>2</sup> However, for the nucleation of CVD diamond on nondiamond substrates, surface relaxation of diamond grains could affect the nucleation barrier energy.<sup>5</sup> Moreover, the nucleation of CVD diamond is originally involved in the physical process.<sup>6,12–15</sup> Theoretically, thermodynamic nucleation has been validly employed to deal with diamond phase formation on nondiamond substrates upon CVD.<sup>13–15</sup> Experimentally, more experimental data implied that CVD diamond concerns physical nucleation.<sup>5–6</sup> Especially, Wang et al. studied the heterogeneous nucleation of CVD diamond in experimental and thermodynamic in detail, and reported that the thermodynamic calculations were in good

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agreement with experimental data.<sup>16</sup> Accordingly, thermodynamic nucleation could be valid in the formation of diamond phase on nondiamond substrates upon CVD. Nevertheless, most investigations concerning CVD diamond nucleation were focused on those chemical processes in the last 20 years, and only a few of the studies were involved in physical processes of CVD diamond nucleation.<sup>2</sup> Therefore, the study of thermodynamic nucleation of CVD diamond may open another door to gaining insight into diamond nucleation. In this paper, taking the effect of nanosize-induced additional pressure on Gibbs free energy of diamond nuclei and phase transition probability from graphite to diamond into account, we propose a simple thermodynamic approach in nanoscale to gain a better understanding of nucleation of CVD diamond on nondiamond surfaces. Interestingly, on the basis of the model, the novel results that are consistent with basic experiment evidences were deduced. This theory was formulated on the basis of the following assumptions: (i) nano-nuclei are perfectly spherical cap with no structural deformation of the internal structure from the bulk one; (ii) nano-nuclei are mutually noninteractive; (iii) the interface between the diamond nucleus and the nondiamond surface is a incoherent interface.

## II. Nanothermodynamic Model

In the nucleation stage of an atom cluster in the gases, the phase stability is quite different from that of the phase diagram that is determined at atmospheric pressure, as the nuclei are under high-pressure arising from so-called "capillarity", which is expressed by the Laplace-Young equation.<sup>17</sup> For the applications of the Laplace-Young equation in nanoscale, in theory, Hwang et al. compared the chemical potential of diamond with that of graphite upon CVD by employing the Laplace-Young equation for the stability of the nuclei, and indicated that the chemical potential of carbon between diamond and graphite was shown to be reversed when the size of the carbon cluster is sufficiently small (in nanoscale).<sup>14–15</sup> Experimentally, Gao and Bando used the Laplace-Young equation to study the thermal expansion of Ga in carbon nanotubes.<sup>18</sup> Especially, the Laplace-Young equation has been extensively developed to study the formation and phase transition of quantum dots in nanoscale.<sup>19</sup> For instance, Alivisatos et al. studied the structural transformation of CdSe nanocrystals with the radius of 1.0 to 2.1 nm in experimental and thermodynamic in detail.<sup>20</sup> They found that the phase transition pressure of nanocrystals vary from 3.6 to 4.9 GPa for crystallite ranging from 1.0 to 2.1 nm in radius, respectively, in comparison to the value of 2.0 GPa for bulk CdSe. Furthermore, they reported that, in this way, the surface energy, taking nanosize-induced additional pressure of nanocrystals into account, could be used to understand the dynamic microscopic path followed by atoms during phase transition. Eventually, those calculations based on the Laplace-Young equation were fully supported by experimental data.<sup>20</sup> Accordingly, it is reasonable for our case to employ the Laplace-Young equation to study the nucleation of CVD diamond on nondiamond surfaces in nanoscale, because the radius of diamond nuclei is in the range of 1 to 3 nm in our case. Now, we discussed the real influence of the additional pressure on the stability of diamond phase from the Laplace-Young equation in detail. Under the assumption of spherical and isotropic nanocrystalline diamond, the sized-induced additional pressure  $\Delta P$  is given by the Laplace-Young equation:  $\Delta P = 2\gamma/r$ , where  $\gamma = 3.7 \text{ J/m}^2$ . The size  $r$  dependence of the additional pressure  $\Delta P$  was shown in Figure 2. One can see that the additional pressure increases as the crystal particle's size decreases.



**Figure 2.** The relationship between the nanosize-induced additional pressure and nuclei size.

Notably, in the radius of diamond particles less 4 nm, the additional pressure goes up to above 2.0 GPa that is above the **B–S** line shown as the **C** region in Figure 1. In other words, the nanosize-induced additional pressure could drive the metastable phase region (**A** region) of diamond nucleation into the new stable phase region (**C** region) in the  $P$ – $T$  phase diagram of carbon. Therefore, the nucleation of CVD diamond on nondiamond surfaces should take place in the stable phase region (**C** region) of diamond when the radius of diamond nuclei is less than 4 nm, based on our nanothermodynamic approach. Importantly, these deductions could obtain experimental support from CVD diamond nucleation on a nondiamond substrate.<sup>5–6</sup> For instance, Lee et al. reported that the size (diameter) of CVD diamond nuclei on Si substrate was in the range of 2–6 nm.<sup>6</sup> Consequently, the nanosize-induced additional pressure of diamond nuclei with the radius of 1–3 nm would be enough to drive the **A** region into the **C** region in Figure 1. In detail, carbon clusters with  $\text{sp}^3$  bonding configuration could form on the surface by a series of surface chemical reactions when carbon atoms diffuse on nondiamond surfaces upon CVD. For instance, the presence of the atomic hydrogen etching graphite phase and helping  $\text{sp}^3$  hybridization of carbon atom could result in the conversion from  $\text{sp}^2$  bonding to  $\text{sp}^3$  bonding of adatoms. Due to the effect of the nanosize-induced additional pressure above on carbon clusters, the thermodynamic environment of carbon cluster formation could be driven from the metastable phase region of diamond into the new stable phase of diamond in the carbon diagram as shown in Figure 1. In this way, in the new stable phase region of diamond, diamond nucleation will occur on nondiamond surfaces by phase transition when the size of carbon clusters goes up to the critical size of the diamond nucleus by trapping neighbor adatoms. In other words, diamond nucleation is preferable to graphite phase formation in the new stable phase region, because this region belongs to stable phase region of diamond. Moreover, for the homoepitaxial growth of diamond on the surface of single-crystalline diamonds upon CVD, diamond nucleation seems not to be taking place. Therefore, CVD diamond could homoepitaxially grow on a surface of single crystalline diamonds by atomic hydrogen etching graphite phase and helping  $\text{sp}^3$  hybridization in the metastable phase region of diamond (**A** region in Figure 1). Additionally, although it has been substantiated that surface chemical processes are the main factor to cause CVD diamond growth on nondiamond surfaces, we must point out that the pressure change should be involved during diamond nucleation.

**A. Heterogeneous Nucleation of CVD Diamond.** According to thermodynamic nucleation,<sup>21</sup> the Gibbs free energy difference, arising from the formation of the spherical cap of diamond clusters on a Si substrate upon CVD, is expressed as

$$\Delta G(r) = V_s/V_m \times \Delta g + (A_{sf}\gamma_{sf} + A_{sc}\gamma_{sc} - A_{cf}\gamma_{cf}) \quad (1)$$

where  $V_s$  and  $V_m$  are the volume of the spherical cap of diamond clusters and mole volume of diamond, respectively.  $\Delta g$  is the mole volume Gibbs free energy difference depending on pressure  $P$  and temperature  $T$  in the phase transition of graphite to diamond.  $A_{sf}$  and  $\gamma_{sf}$  are the interface area and energy between the spherical cap of diamond clusters and gas phase,  $A_{sc}$  and  $\gamma_{sc}$  are the interface area and energy between the spherical cap of diamond clusters and substrates, and  $A_{cf}$  and  $\gamma_{cf}$  are the interface area and energy between substrates and gas phase, respectively. Naturally, the formation of the spherical cap of diamond clusters produces two interfaces, i.e., the interface  $A_{sf}$  between the spherical cap and gas phase and interface  $A_{sc}$  between the spherical cap and substrate, and makes the original interface  $A_{cf}$  (equal to  $A_{sc}$ ) between substrate and gas phase vanish. According to the geometry, the volume  $V_s$  of the spherical cap of diamond clusters, the interface area  $A_{sf}$  between the spherical cap and gas phase and interface area  $A_{sc}$  between the spherical cap and substrate are expressed as  $V_s = \pi r^3/3(2 + m)(1 - m)^2$ ,  $A_{sf} = 2\pi r^2(1 - m)$ ,  $A_{sc} = \pi r^2(1 - m^2)$ , respectively, where  $r$  is the curvature radius of the spherical cap of diamond clusters.  $m$  is given by  $m = \cos \theta = (\gamma_{cf} - \gamma_{sc})/\gamma_{sf}$ , where  $\theta$  is the contact angle between the spherical cap of diamond clusters and substrates. In our case,  $\gamma_{sf}$  is assumed to be approximately equal to the surface free energy value of diamond of 3.7 J/m<sup>2</sup>,<sup>11</sup>  $\gamma_{cf}$  for the interface energy between Si substrate and gas phase is taken to be equal to the surface energy value of silicon of 1.24 J/m<sup>2</sup>, and the interface between the spherical cap of diamond clusters and Si substrate is assumed to be incoherent interface. Thus,  $\gamma_{sc} = (\gamma_{sf} + \gamma_{cf})/2$ . Then, we obtain

$$\Delta G(r) = \left[ \frac{4}{3}\pi r^3 \times \Delta g/V_m + 4\pi r^2 g_{sf} \right] (2 + m)(1 - m)^2/4 \quad (2)$$

where the factor of  $f(\theta) = (2 + m)(1 - m)^2/4$  is called the heterogeneous factor. According to thermodynamics, we obtain  $(\partial \Delta g_{T,P}/\partial P)_T = \Delta V$ . Then,  $\Delta g_{T,P} = \Delta g^0_T + \int_0^P \Delta V dP$ , where  $\Delta V$  is mole volume difference between graphite and diamond, and  $\Delta g^0_T$  is mole Gibbs free energy difference at zero pressure, respectively. Bundy's experimental results showed that  $\Delta V$  remains approximately constant with pressure–temperature condition, i.e.,  $\Delta V = 1.77 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$ .<sup>11</sup> Under the assumption of spherical and isotropic nanocrystalline diamond, the size-induced additional pressure  $\Delta P$  is given by the Laplace–Young equation:  $\Delta P = 2\gamma/r$ , where  $\gamma = 3.7 \text{ J/m}^2$ . According to Figure 1, the equilibrium phase boundary between graphite and diamond, the so-called **B–S** line, in the pressure–temperature phase diagram of carbon is expressed by  $P^e = 2.73 \times 10^6 T + 7.23 \times 10^8$ . Due to the additional pressure  $\Delta P$ , the external pressure  $P^e$  being necessary for the transition of graphite to diamond will decrease by the same amount, i.e.,  $P^e = P^e + 2\gamma/r$ . Thus, one can obtain the size-dependent equilibrium phase boundary:  $P^e = 2.73 \times 10^6 T + 7.23 \times 10^8 - 2\gamma/r$  (Pa). When the conditions are on the equilibrium line, one has  $\Delta g_{T,P} = 0$ . Then, one can attain mole volume Gibbs free energy difference of the graphite to diamond transition:

$$\Delta g^d_{T,P} = \Delta V \times (P - 2.73 \times 10^6 T - 7.23 \times 10^8 + 2\gamma/r) \quad (3)$$

According to the thermodynamic discussion above, the Gibbs free energy difference of the phase transition from graphite to diamond considering the size-induced additional pressure effect is

$$\Delta G(r) = \left[ \frac{4}{3}\pi r^3 \Delta V \times (P - 2.73 \times 10^6 T - 7.23 \times 10^8 + 2\gamma/r)/V_m + 4\pi r^2 \gamma \right] (2 + m)(1 - m)^2/4 \quad (4)$$

When  $(\partial \Delta G(r)/\partial r) = 0$ , the critical size of diamond nuclei is obtained as

$$r^* = 2\gamma \left( \frac{2}{3} + \frac{V_m}{\Delta V} \right) / (2.73 \times 10^6 T + 7.23 \times 10^8 - P) \quad (5)$$

Substituting eq 5 into eq 4, the critical energy of diamond nuclei is given by

$$\Delta G(r^*) = \left[ \frac{4}{3}\pi r^{*3} \Delta V \times (P - 2.73 \times 10^6 T - 7.23 \times 10^8 + 2\gamma/r^*)/V_m + 4\pi r^{*2} \gamma \right] (2 + m)(1 - m)^2/4 \quad (6)$$

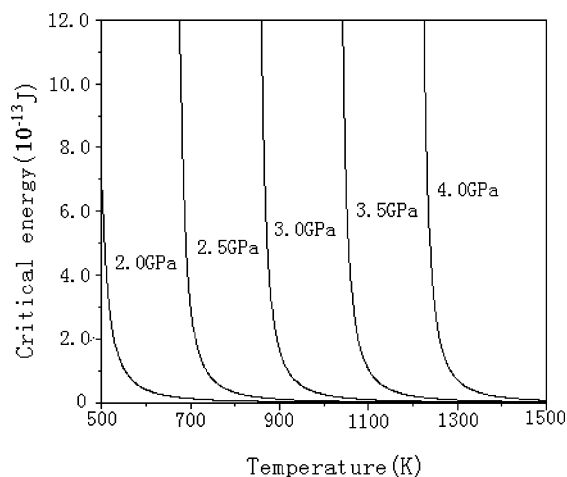
In fact, misfit between diamond nuclei and nondiamond substrates could greatly affect the value of the interface energy  $\gamma_{cf}$ , while a large  $\gamma_{cf}$  could result in a large forming energy of nuclei. Normally, interfaces between nuclei and substrates could be divided into coherent, semicoherent, and incoherent interfaces according to the degree of their lattice mismatch. For various interfaces, the interface energy  $\gamma_{cf}$  could be expressed by  $\gamma_{cf} = \gamma_{\text{chem}} + \gamma_{\text{structure}}$ , where  $\gamma_{\text{chem}}$  means a chemical term from the contribution of the interface chemical bonding and  $\gamma_{\text{structure}}$  is a structure term from the contribution of the elasticity energy of nuclei. It is well-known that the formation of misfit dislocation due to ideal disregistry between nuclei and large substrates could result in the value of the structure term  $\gamma_{\text{structure}}$  increasing, further, promoting the value of interface energy  $\gamma_{cf}$ .<sup>22</sup> Therefore, the critical size of diamond nuclei is different when diamond nucleation occurs on different nondiamond substrates. Furthermore, the small ideal disregistry means the small contact angle, critical size, and forming energy of nuclei. Eventually, diamond nucleation preferably takes place on the nondiamond surface where the interface energy is small.

**B. Phase Transition from Graphite to Diamond upon CVD.** Since the phase transition from graphite to diamond is determined quantitatively by the probability of the carbon atoms crossing a potential barrier of intermediate phase in the  $P$ – $T$  phase diagram of carbon,<sup>23</sup> we studied the nanosize-effect on the probability of the phase transformation based on the  $P$ – $T$  phase diagram. The probability of the phase transformation from the metastable phase to the stable phase is related not only to the Gibbs free energy difference  $\Delta g_{T,P}$ , but also to an activation energy ( $E_a - \Delta g_{T,P}$ ) that is necessary for the transition. When the two phases are at the equilibrium condition, i.e.,  $\Delta g_{T,P} = 0$ ,  $E_a$  is the maximum potential energy for both sides with respect to the general coordinate. The general expression of the probability  $f$  of the phase transformation from the initial states to final states is<sup>23</sup>

$$f = \exp[-(E_a - \Delta g_{T,P})/RT] - \exp[-(E_a/RT)] \quad (7)$$

where  $R$  is the gas constant. For the phase transformation from graphite to diamond,  $f = f_d$  and  $\Delta g^d_{T,P} = g^e_{T,P}$  (graphite) –  $g^d_{T,P}$  (diamond), and ( $E_a - \Delta g^d_{T,P}$ ) is the activation energy of the graphite to diamond transition.  $f_d$  can be therefore given by





**Figure 3.** The dependence of the forming energy of CVD diamond nuclei on the temperature under conditions of various nanosize-induced additional pressures.

eq 7. Instead, for the phase transformation from diamond to graphite,  $f = f_g$  and  $\Delta g_{T,P}^g = g_{T,P}^d(\text{graphite}) - g_{T,P}^d(\text{diamond})$ ,  $f_g$  should be expressed as

$$f_g = \exp[-(E_a/RT)] - \exp[-(E_a - \Delta g_{T,P}^g)/RT] \quad (8)$$

It is noticed that, for the phase transition of diamond to graphite,  $\Delta V = -1.77 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$ , and the mole volume Gibbs free energy difference  $\Delta g_{T,P}^g$  can be given by

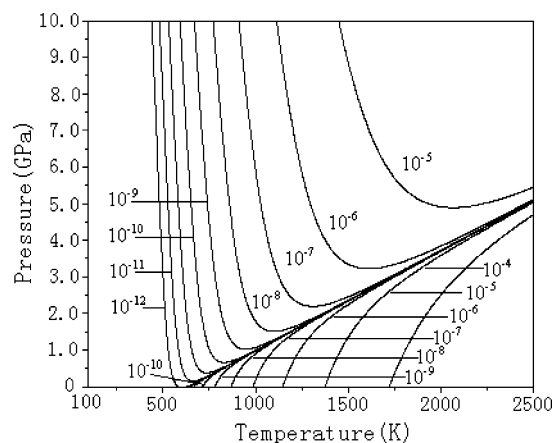
$$\Delta g_{T,P}^g = 1.77 \times 10^{-6} (2.73 \times 10^6 T + 7.23 \times 10^8 - 2\gamma/r - P) \quad (9)$$

### III. Results and Discussions

According to eq 6 and  $V_m = 3.417 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$ ,<sup>23</sup> we calculated the temperature dependence of the Gibbs free energy of diamond nuclei considering the nanosize effect in the temperature range of 500 to 1500 K, and the results were shown in Figure 3. Clearly, one can see in Figure 3 that the energy of formation of diamond nuclei decreases with increasing temperature at a given pressure, and increases with the increasing pressure. These results showed that heterogeneous nucleation of CVD diamond does not need high forming energy from our calculations. Apparently, the low forming energy of heterogeneous nucleation of CVD diamond implied that it is not difficult for diamond nucleation to take place, further, diamond nucleation should happen in the stable phase region (C region) of diamond as shown Figure 1.

According to eqs 7 and 8, and  $E_a = 120 \text{ kJ mol}^{-1}$ ,<sup>23</sup> we calculated the probability curves of the graphite–diamond transition in the new stable phase region of diamond (C region in Figure 1) in the phase diagram of carbon when  $r = 3.0 \text{ nm}$  as shown in Figure 4. One can see in Figure 4 that the probability of the phase transition from graphite to diamond is about  $1.0 \times 10^{-7}$  to  $1.0 \times 10^{-6}$  in the new stable phase region. Actually, the probabilities of graphite to diamond transition,  $1.0 \times 10^{-7}$  to  $1.0 \times 10^{-6}$ , are really low in the C region.

On the other hand, from Figure 1 and Figure 2, we can also see an inverse process where the thermodynamic environment of the growth of diamond nuclei would drop down from the stable phase region of diamond (C region) to the metastable phase region (A region) when the size of diamond nuclei gradually grows up on CVD. For example, the growth of diamond nuclei will be in the region below the B–S line when



**Figure 4.** The probability of phase transition of graphite to diamond with respect to the effect of nanosize-induced additional pressure in the new stable phase region (C region in Figure 1) of CVD diamond nucleation (above the B–S line).

the radius of diamond nuclei is larger than 4 nm. Meanwhile, the growth of the graphite phase will be preferable to diamond phase formation. More importantly, Winter and Ree calculated carbon particle phase stability as a function of size by first-principles and semiempirical molecular orbital calculations.<sup>24</sup> Their results showed that the diamond phase is more stable than the graphite phase when carbon particle include less than  $10^4$ – $10^5$  carbon atoms. However, diamond clusters larger than  $10^5$  carbon atoms become less stable than three-dimensional graphite clusters of the same size. Actually, in the case of the incoherent interface between diamond nuclei and silicon substrate, the size (diameter) of the spherical cap of diamond nuclei including  $10^5$  atoms on silicon surfaces is about 8 nm. Thus, our deductions above are in agreement with Winter and Ree's calculations. Accordingly, nucleation of diamond and growth of diamond nuclei would take place in two different thermodynamic phase regions based on our model. Diamond nucleation takes place in the stable phase of diamond, differently, growth of diamond nuclei including homoepitaxially growth of CVD diamond on a surface of single crystal diamonds occurs in the metastable phase of diamond, due to the nanosize effect induced by the curvature-surface tension. Definitely, these results showed that, to promote nucleation density of diamond on nondiamond surfaces, the deposition parameters of CVD employed in the stage of diamond nucleation should be greatly different from that employed in the stage of the growth of diamond nuclei. Notably, these deductions are consistent with the experimental evidence below.

On the other hand, why did most experimental studies show that atomic hydrogen played a very important role in CVD diamond? According to the results above, it would not be easy to induce CVD diamond nucleation due to the low probability of phase transition of graphite to diamond ( $1.0 \times 10^{-7}$  to  $1.0 \times 10^{-6}$ ) in the C region in Figure 1. In fact, it is recognized experimentally that atomic hydrogen etching graphite phase more etching rate to graphite phase and less etching rate to diamond phase and helping  $\text{sp}^3$  hybridization of carbon atom.<sup>2</sup> Naturally, the formation of diamond nuclei could be enhanced upon CVD, only when graphite phase forming is restrained or stopped by atomic hydrogen or other factors. In other words, the presence of atomic hydrogen aids diamond nuclei formation. However, the presence of atomic hydrogen could not promote the nucleation density of diamond on nondiamond surfaces due to its also etching diamond phase. Actually, the effect of atomic hydrogen on the growth of CVD diamond nuclei is much greater

than that on the formation of diamond nuclei.<sup>25</sup> For instance,<sup>26</sup> to promote nucleation density of CVD diamond, the carbon concentration of the reactant gases such as CH<sub>4</sub>/H<sub>2</sub> at the stage of diamond nucleation can be much higher, up to 10 to 20%. Then, the carbon concentration at the stage of diamond growth is usually less 1% in the reactant gases. Therefore, these results implied that the influence of atomic hydrogen on diamond nucleation would not be really important based on those experimental studies involved in enhancing CVD diamond nucleation.<sup>26</sup> Additionally, we expected the new experiments to substantiate those deductions above.

#### IV. Conclusion

Aiming at a clear insight into heterogeneous nucleation of CVD diamond, we studied diamond nucleation from the point of the view of nanoscaled thermodynamics. Notably, these results showed that diamond nucleation would happen in the stable phase region of diamond in the carbon phase diagram, due to the nanosize effect induced by the curvature-surface tension of diamond nuclei. In other words, in nanoscale, diamond nucleation is prior to graphite nucleation in competing growth of diamond and graphite upon CVD. Furthermore, we expect the nanothermodynamic analyses to be a general approach to elucidate nucleation of diamond and related materials in low-temperature and low-pressure gas phase.

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