

## Nucleation Thermodynamics of Cubic Boron Nitride upon High-Pressure and High-Temperature Supercritical Fluid System in Nanoscale

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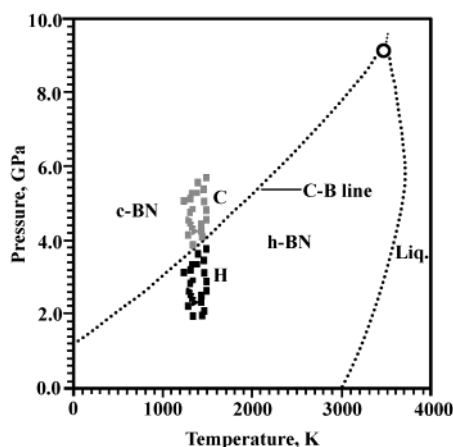
Based on the boron nitride thermodynamic equilibrium phase diagram, a thermodynamic analysis in nanoscale was proposed, with respect to the effect of nanosize-induced additional pressure on Gibbs free energy of critical nuclei of cubic boron nitride (c-BN), to elucidate nucleation of c-BN in a high-pressure and high-temperature (HPHT) supercritical fluid system. Notably, our analysis showed that the effect of surface tension induced by the nanosize curvature of critical nuclei could drive the metastable phase region of c-BN nucleation into stable phase region in the phase diagram. Consequently, c-BN nucleation would be prior to hexagonal boron nitride (h-BN) nucleation in competing growth of c-BN and h-BN upon HPHT supercritical fluid system.

Since the first successful synthesis of c-BN by high-pressure and high-temperatures (HPHT) method with  $\text{Li}_3\text{N}$  as a catalyst, which is similar to the synthesis of diamond, was reported in a short note by Wentorf in 1957,<sup>1</sup> more detailed investigations had followed by Wentorf, Corrigan, and Bundy.<sup>2–4</sup> It is well-known that c-BN is the simplest and pure artificial III–V compound. Therefore, the material has attracted great interest due to its enormous potential for technological applications.<sup>5</sup> For the basic physical process concerned in c-BN synthesis by HPHT, it is generally thought that the thermodynamically stable phase is hexagonal boron nitride (h-BN) under the conditions of normal pressure and temperature based on the general accepted phase diagram proposed by Corrigan and Bundy.<sup>4</sup> Then, c-BN would be only synthesized in those phase regions, in which c-BN is stable phase and h-BN is metastable phase; that is, those phase regions are located above the Corrigan-Bundy boundary line (C-B line) in the boron nitride thermodynamic equilibrium phase diagram. Furthermore, Bundy and Wentorf pointed out that the direct transformation from h-BN to c-BN without catalyst would realize in the HPHT case.<sup>3</sup> Actually, up to date, most experimental and theoretical investigations of c-BN synthesis by HPHT have been basically restricted within the outline above.<sup>6</sup> However, very recently, the important progress of c-BN synthesis by HPHT, which was developed by Solozhenko and Singh et al., seems breaking the Corrigan-Bundy's fence. Solozhenko and Singh et al. first synthesized c-BN under supercritical conditions using nonconventional catalysts such as the volatile hydrazine  $\text{NH}_2\text{NH}_2$  and  $\text{MgB}_2$ <sup>7</sup> (so-called HPHT supercritical fluid system) in the phase region that the pressure is in the range of 1.8–3.8 GPa and the temperature is in the range of 1200–1600 K by HPHT.<sup>8–12</sup> Importantly, these phase regions are located below the C-B line of the boron nitride thermodynamic equilibrium phase diagram, in which the c-BN phase would be metastable and the h-BN phase would be stable. In other words, c-BN synthesis would not be expected upon HPHT in those phase regions. Therefore, according to the experiments and theoretical calculations based on a series of hypotheses, Solozhenko et al. suggested that the

C-B line would move down in the boron nitride thermodynamic equilibrium phase diagram developed by Corrigan and Bundy. Furthermore, they proposed a new boron nitride thermodynamic equilibrium phase diagram to substitute for the Corrigan-Bundy equilibrium phase diagram.<sup>7,13–15</sup> Would the Corrigan-Bundy equilibrium phase diagram be really outdated for c-BN synthesis by HPHT? In fact, it is an essential issue involved in the fundamental thermodynamics in the HPHT supercritical fluid system of c-BN synthesis. To our best knowledge, there are hardly any the thermodynamic descriptions concerned in HPHT supercritical fluid system,<sup>6</sup> because the full understanding of the complicated interactivities during nonconventional catalyst/solvent synthesis has not been obtained in detail yet. To gain a better understanding of c-BN nucleation in the HPHT supercritical fluid system from the point of the view of thermodynamics, in this paper, a thermodynamics analysis in nanoscale was proposed, with respect to the effect of nanosize-induced additional pressure on Gibbs free energy of critical nuclei, to have a clear insight into microscopic process of c-BN nucleation in the HPHT supercritical fluid system. It is emphasized that the effect of surface tension, so-called the nanosize-induced additional pressure,<sup>16,17</sup> on Gibbs free energy of critical nuclei should be reasonably taken into account in the deduction below, as the nucleation of c-BN synthesis upon HPHT supercritical fluid system would be limited in nanometer scale.<sup>18</sup> However, the key point has not been taken into account in the previous relevant researches yet.<sup>6</sup>

In fact, the nucleation and growth of c-BN are complicated in a flux of another material (so-called “catalyst”) upon HPHT supercritical fluid system. Generally, c-BN is considered to be spontaneous crystallization in the so-called conventional “solvents-catalysts system”.<sup>19</sup> Actually, no matter what in the conventional solvents-catalysts system or the supercritical fluids system, the nucleation and growth of c-BN must meet simultaneously the conditions as follows: (i) the raw material and catalyst molten in the system, (ii) the high-supersaturation raw material in the solvent catalysts, and (iii) the ambient pressure (including the nanosize induced additional pressure) and temperature of the spontaneous-crystallization of c-BN clusters above C-B line (or the spontaneous-crystallization of c-BN clusters are unstable

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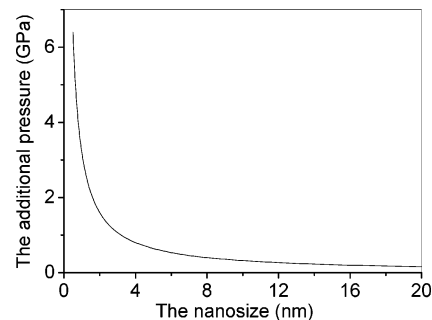


**Figure 1.** Boron nitride thermodynamic equilibrium phase diagram. The H region means a metastable phase region of c-BN nucleation; The C region means a new stable phase region of c-BN nucleation with respect to the effect of nanosize-induced additional pressure (the data of the square symbols of the H region is derived from ref 14).

else). However, the results of Solozhenko and Singh et al.<sup>8–12</sup> showed the nucleation and growth of c-BN in a wide temperature and pressure range in the supercritical fluids system (as shown in Figure 1. H region). Then, the case would be impossible in a conventional solvents–catalysts system. Thus, it is reasonable that the structure of the resulting solutions and the mechanism of BN crystallization from these solutions are expected to be heavily dependent on the fluid phase composition. Naturally, the results are incompatible with the general accepted phase diagram proposed by Corrigan and Bundy.

On the other hand, it is well-known that, because c-BN was synthesized by HPHT, many models have discussed the nucleation and growth of c-BN. However, each model tends to focus on the certain experiments of c-BN synthesis. For example, the solid–solid transition model thinks that h-BN melts in catalyst solvent under the certain conditions of the pressure and temperature, then, the formation of the new solvent (BN-rich). Subsequently, the temperature increasing leads to the formation of a second compound that is more BN-rich compared with that mentioned above. Finally, the new BN-rich compound formed under high pressures and temperatures becomes unstable and decomposes into c-BN and another product (unknown structure and composition yet) by a fast solid–solid transition process.<sup>20</sup> However, very recently, Solozhenko<sup>21</sup> reported that the formation of any crystalline intermediate phases was not observed from beginning to the onset of the c-BN crystallization in  $\text{NH}_4\text{F}$ –BN system, and only h-BN and a melt coexist in the system by in situ measuring using X-ray diffraction with synchrotron radiation. These results made us revise the solid–solid transition model and allowed us to draw some conclusions about the mechanism of the nucleation and growth of c-BN in the supercritical fluids. This study is the first attempt to employ the developed heterogeneous gas-phase nucleation theory (taking sufficient account of the surface-induced internal pressure in the nanoscale region) as a qualitative analysis of the nucleation and growth of c-BN in the supercritical fluids system.

Generally, in the case of the nucleation of a cluster from 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” that is expressed by the Laplace–Young equation.<sup>22</sup> For the applications of the Laplace–Young equation in the nanoscale region, theoretically, Hwang et al. compared the chemical



**Figure 2.** Relationship curve between the nanosize-induced additional pressure and nuclei size based on the Laplace–Young equation:  $\Delta P = 2\gamma/r$ .

potential of diamond with that of graphite upon chemical vapor deposition 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 the nanoscale region).<sup>23</sup> Experimentally, Gao and Bando used the Laplace–Young equation to study the thermal expansion of Ga in carbon nanotubes.<sup>16,17</sup> Especially, the Laplace–Young equation in the nanoscale region has been extensively developed to study the formation of quantum dots.<sup>16,17,24</sup> For instance, Alivisatos et al. discussed the elevation of pressure in the solid–solid structural transformation as crystallite size (in nanoscale) decreases in a high-pressure system using the Laplace–Young equation.<sup>24</sup> Accordingly, it is reasonable that the Laplace–Young equation would be used to investigate the c-BN nucleation upon the HPHT supercritical fluid system from the point of the view of thermodynamic nucleation, as the supercritical fluid may have liquidlike densities but gaslike properties.<sup>25</sup> The boron nitride thermodynamic equilibrium phase diagram (the general accepted one by Corrigan–Bundy given in 1975) is shown in Figure 1. The general phase region of c-BN synthesized upon the HPHT supercritical fluid system was shown as the H region of Figure 1. Obviously, the phase region belongs to the metastable region of the c-BN phase, i.e., the stable region of the h-BN phase based on the Corrigan and Bundy defined phase boundary (C-B line). However, would c-BN nucleation be really in the metastable phase region of c-BN in the phase diagram upon HPHT under the conditions of the supercritical fluid? For this issue, now, we discuss the real influence of the additional pressure from the Laplace–Young equation in detail. Under the assumption of spherical and isotropic c-BN nanocrystals, the sized-induced additional pressure  $\Delta P$  was given by the Laplace–Young equation:  $\Delta P = 2\gamma/r$ , where  $\gamma$  ( $\gamma = 1.6 \text{ J/m}^2$ ) is the specific free surface energy of the crystal–melt interface.<sup>26</sup> The size  $r$  dependence of the additional pressure  $\Delta P$  was shown in Figure 2. Clearly, one can see that the additional pressure increases with the crystal particle’s size decreasing from Figure 2. Notably, in the size range below 1.6 nm, the additional pressure goes up to above 2.0 GPa that is above the C-B line shown as the C region in Figure 1,<sup>14</sup> in which the c-BN phase is stable. In other words, if only the size of the c-BN nucleation is in the range from 1.6 to 8 nm, the nanosize-induced additional pressure could drive the metastable region (H region) of c-BN nucleation into the new stable region (C region) in the P–T phase diagram of boron nitride. Substantially, these deductions could obtain the experimental cases from c-BN nucleation upon the HPHT supercritical fluid system.<sup>18</sup> For instance, Horiuchi et al., reported that the size of c-BN nuclei in the HPHT supercritical fluid system was in the range of 2–8 nm.<sup>18</sup> Consequently, the nanosize-induced additional pressure of the

c-BN nuclei with the radius of 2–5 nm would be enough to drive the H region into the C region in Figure 1. Following these discussions, we will give a thermodynamic analysis of c-BN nucleation in the  $\text{NH}_2\text{NH}_2\text{-BN-MgB}_2$  system by HPHT.

Normally, in the case of the heterogeneous nucleation, a spherical and isotropic crystal with the radius of  $r$  is surrounded by its melt. The energy of the formation of a spherical nucleus from the melt is<sup>27</sup>

$$E_G = \left( \frac{4}{3}\pi r^3 \times \Delta\mu/V_m + 4\pi r^2\gamma \right) (1 - \cos\theta)^2(2 + \cos\theta)/4 \quad (1)$$

where  $V_m$  is the mole volume of c-BN,  $\gamma$  is the specific free surface energy of the crystal–melt interface,  $\theta$  is a contact angle,  $\Delta\mu$  is the difference per mole in the chemical potential between the substance in the melt and in the solid phase under the  $P$  and  $T$  conditions of crystallization, respectively. As in the course of dissolution of h-BN in the melt of the Mg–B–N system, this melt becomes saturated and the liquid phase proves to be in the equilibrium with undissolved h-BN, and then, the equations  $\mu_{\text{h-BN}} = \mu_{\text{BN}}$ , and  $\Delta\mu = \mu_{\text{c-BN}} - \mu_{\text{h-BN}}$  are valid.<sup>28</sup> The condition for the equilibrium is that  $E_G$  is at an extremum for a variation  $dr$  of the radius

$$\frac{dE_G}{dr} = (4\pi r^2 \Delta\mu/V_m + 8\pi r\gamma)(1 - \cos\theta)^2(2 + \cos\theta)/4 = 0 \quad (2)$$

This gives the condition for the radius of curvature

$$r^* = - \frac{2\gamma V_m}{\Delta\mu} \quad (3)$$

In our further calculations, we used the  $\gamma$ ,  $V_m$ , and  $\Delta\mu$  dependences found from the data on the thermodynamic properties of boron nitride.<sup>29</sup> Taking into account the data reported in ref 26 and 30,  $g$  was assumed to be 1.6 J/m<sup>2</sup>, the mole volume of c-BN  $V_m = 7.123 \times 10^{-6}$  m<sup>3</sup>/mol, and  $\Delta\mu$  was assumed to be 1.3–9.2 = −7.9 kJ/mol, respectively. Under these assumptions, the radius of the curvature of the critical nucleation is about 2.8 nm. Therefore, c-BN nucleation in the supercritical fluid system by nonconventional catalysts should happen in the C region in Figure 1, based on our thermodynamic calculation above in nanoscale.

It is well-known that the Gibbs free energy is an adaptable measure of the energy of a state in phase transformation among competing phases. Under the given thermodynamic condition, both c-BN and h-BN phases can coexist, but only one of the two phases is stable, with minimal free energy, and the other must be metastable and may transform into the stable state. Thermodynamically, the phase transformation is promoted by the difference of the free energies. The Gibbs free energy of a phase can be expressed as a function of the pressure–temperature condition and determined by a general coordinate or reactive coordinate. According to the nucleation thermodynamics,<sup>31</sup> the Gibbs free energy of spherical c-BN clusters (in an earlier study, c-BN clusters were found effectively stabilized by having equal numbers of B and N atoms<sup>32</sup>) is expressed as a function of radius  $r$ , pressure  $P$ , and temperature  $T$  in the supercritical fluid system as follows:

$$\Delta G(r, P, T) = V_s/V_m \Delta g_{T,P} + (A_{\text{sm}}\gamma_{\text{sm}} + A_{\text{sf}}\gamma_{\text{sf}} - A_{\text{fm}}\gamma_{\text{fm}}) \quad (4)$$

Where  $V_s$  and  $V_m$  are the volume of spherical c-BN clusters

and the mole volume of c-BN, respectively,  $\Delta g$  is the mole volume Gibbs free energy depending on pressure  $P$  and temperature  $T$  in the phase transition,  $A_{\text{sm}}$  and  $\gamma_{\text{sm}}$  are the interface area and energy between spherical cap of c-BN clusters and the melt,  $A_{\text{sf}}$  and  $\gamma_{\text{sf}}$  are the interface area and energy between spherical cap of c-BN clusters and the flux precursor, and  $A_{\text{fm}}$  and  $\gamma_{\text{fm}}$  are the interface area and energy between the flux precursor and the melt. The formation of spherical c-BN clusters produces two interfaces, i.e., the interface  $A_{\text{sm}}$  between spherical cap and the melt and the interface  $A_{\text{sf}}$  between spherical cap and the flux precursor, and makes the original interface  $A_{\text{fm}}$  that is equal to  $A_{\text{sm}}$  between the flux precursor and the melt vanish. According to the common sense of geometry, the volume  $V_s$  of spherical c-BN clusters, the interface area  $A_{\text{sm}}$  between spherical cap and the melt, and the interface area  $A_{\text{sf}}$  between spherical cap and the flux precursor are expressed as,  $V_s = \pi r^3 / 3(2 + m)(1 - m)^2$ ,  $A_{\text{sm}} = 2\pi r^2(1 - m)$ , and  $A_{\text{sf}} = \pi r^2(1 - m^2)$ , respectively, where  $r$  is the curvature radius of spherical cap of c-BN clusters and  $m$  is given by  $m = \cos\theta = (\gamma_{\text{fm}} - \gamma_{\text{sf}})/\gamma_{\text{sm}}$ , where  $\theta$  is the contact angle between the spherical cap of c-BN clusters and the melt. In this paper, taking into account the data reported in ref 26,  $\gamma_{\text{sm}}$  is assumed to be 1.6 J/m<sup>2</sup> and the contact angle  $\theta = 30^\circ$ . Thus, we obtain

$$\Delta G(r, P, T) = \left[ \frac{4}{3}\pi r^3 \times \Delta g_{T,P}/V_m + 4\pi r^2\gamma_{\text{sm}} \right] \times (2 + \cos\theta)(1 - \cos\theta)^2/4 \quad (5)$$

where the factor of  $f(\theta) = (2 + \cos\theta)(1 - \cos\theta)^2/4 = 0.05$  is called the heterogeneous factor.

According to the value of  $f(\theta)$ , eq 5 is expressed as

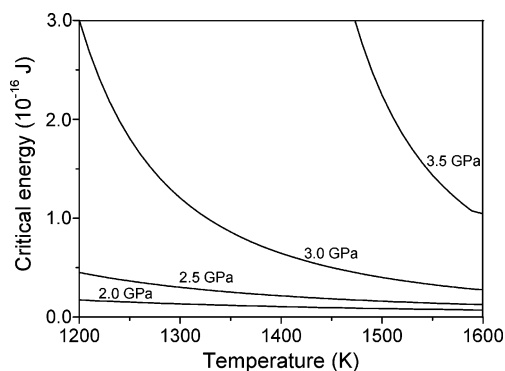
$$\Delta G(r, P, T) = \left[ \frac{4}{3}\pi r^3 \Delta g_{T,P}/V_m + 4\pi r^2\gamma_{\text{sm}} \right] 0.05 \quad (6)$$

According to thermodynamics, we obtain  $(\partial\Delta g_{T,P}/\partial P)_T = \Delta V$ . Then,  $\Delta g_{T,P} = \Delta g_T^0 + \int_0^P \Delta V dP$  where  $\Delta V$  is the molar volume difference between h-BN and c-BN, and  $\Delta g_T^0$  is the molar Gibbs free energy difference at zero pressure. Bundy's experimental results showed that  $\Delta V$  remains approximately constant with pressure–temperature condition.<sup>33</sup> According to the densities of h-BN and c-BN, we have  $\Delta V = 3.79 \times 10^{-6}$  m<sup>3</sup> mol<sup>−1</sup>. From Figure 1, the C–B line (so-called Corrigan–Bundy's line, namely, the equilibrium phase boundary between h-BN and c-BN) is expressed approximatively by  $P^e = 1.833 \times 10^6 T + 1.117 \times 10^9$ . Due to the additional pressure  $\Delta P$ , the external pressure  $P^e$  necessary for the transition of h-BN to c-BN will decrease by the same amount, i.e.,  $P^e = P^{e0} + 2\gamma_{\text{sm}}/r$ . Thus, one can obtain the size-dependent equilibrium phase boundary:  $P^{e0} = 1.833 \times 10^6 T + 1.117 \times 10^9 - 2\gamma_{\text{sm}}/r$  (Pa). When the conditions are on the equilibrium line, one has  $\Delta g_{T,P} = 0$ ; thus, one can attain molar-volume Gibbs free energy difference of the h-BN to c-BN transition

$$\Delta g_{T,P}^c = \Delta V(P - 1.833 \times 10^6 T - 1.117 \times 10^9 + 2\gamma_{\text{sm}}/r) \quad (7)$$

From eqs 7 and 6, the Gibbs free energy difference of the transition from h-BN to c-BN considering the size-induced additional pressure effect is

$$\Delta G(r, P, T) = \left[ \frac{4}{3}\pi r^3 \Delta V(P - 1.833 \times 10^6 T - 1.117 \times 10^9 + 2\gamma_{\text{sm}}/r)/V_m + 4\pi r^2\gamma_{\text{sm}} \right] 0.05 \quad (8)$$



**Figure 3.** Relationship curve of the formation energy and temperature in various nanosize-induced additional pressure.

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

$$r^* = 2\gamma_{\text{sm}} \left( \frac{2}{3} + \frac{V_{\text{m}}}{\Delta V} \right) / (1.833 \times 10^6 T + 1.117 \times 10^9 - P) \quad (9)$$

Substituting eq 9 into eq 8, the critical energy of c-BN nuclei is given by

$$\Delta G(r^*, P, T) = \left[ \frac{4}{3} \pi r^{*3} \Delta V (P - 1.833 \times 10^6 T - 1.117 \times 10^9 + 2\gamma_{\text{sm}}/r^*)/V_{\text{m}} + 4\pi r^{*2} \gamma_{\text{sm}} \right] 0.05 \quad (10)$$

According to eq 10 and the values of  $\gamma_{\text{sm}}$ ,  $\Delta V$ , and  $V_{\text{m}}$ , we deduced the relationship curve of the formation energy and temperature in various nanosize-induced additional pressure, as shown in Figure 3. Clearly, one can see that the formation energy of the c-BN nuclei decreases with the temperature increasing at a given pressure and increases with the pressure increasing. These results showed that heterogeneous nucleation of c-BN does not need a high formation energy in the supercritical fluid system. Apparently, the low forming energy of heterogeneous nucleation of c-BN implied that it is not difficult for c-BN nucleation in the HPHT supercritical fluid system, and c-BN nucleation would happen in the stable region (the C region) as shown Figure 1.

In summary, aiming at a clear insight into c-BN nucleation in the HPHT supercritical fluid system, we have investigated c-BN nucleation from the point of the view of thermodynamics in the nanoscale region. Notably, a thermodynamic analysis was conducted, taking the effect of nanosize-induced additional pressure on the Gibbs free energy of the critical nucleus into account. The results indicated that c-BN nucleation would happen in the stable region of c-BN in the boron nitride phase

diagram developed by Corrigan and Bundy; that is, c-BN nucleation would be prior to h-BN nucleation in competing growth of c-BN and h-BN in HPHT supercritical system. Consequently, we expect the nanothermodynamic analyses proposed in our case to be a general approach applicable to elucidate nucleation of materials occurring in nanometer scale.

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