Prediction of formation of cubic boron nitride by construction of temperature–pressure phase diagram at the nanoscale

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ABSTRACT

The size-dependent phase diagram of BN was developed on the basis of the nanothermodynamic theory. Our studied results suggest that cubic BN (c-BN) is more stable than hexagonal BN (h-BN) in the deep nanometer scale and the triple point of c-BN, h-BN and liquid shifts toward the lower temperature and pressure with decreasing the crystal size. Moreover, surface stress, which is determined by the experimental conditions, is the main reason to influence the formation of c-BN nuclei. The developed phase diagram of BN could help us to exploit new techniques for the fabrication of c-BN nanomaterials.

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1. Introduction

Boron nitride (BN) is similar to carbon with two crystalline structures: a layered hexagonal structure (h-BN), which is similar to that of graphite, and the cubic zinc-blende structure (c-BN), analogous to that of diamond [1]. Therefore, c-BN shares many similar attractive properties of diamond and shows high potential for mechanical, electrical and optical applications [1,2]. Although c-BN was prepared by the high-pressure and high-temperature method in 1957 [3], many attentions of developing facile and economical c-BN preparations have been paid for 50 years. It is well known that phase diagram is helpful in predicting phase transformations and the resulting microstructures. Accordingly, the pressure–temperature (P–T) phase diagram of BN was attempted to be constructed immediately by Wentorf after his synthesis of c-BN, and then was improved by Corrigan and Bundy in 1963 [4,5]. Subsequently many researchers attempt to refine the BN phase diagram on the basis of experimental data and thermodynamic approach [6–10].

Fig. 1 is the last BN equilibrium phase diagram from Solozhenko et al. [8]. However, this phase diagram cannot explain the phenomena that the formation regions of c-BN nuclei produced from many synthesized methods, such as ion-assisted chemical vapor deposition

(CVD), ion-assisted physical vapor deposition (PVD) [2] and super-critical-fluid system [11,12], are located below the phase equilibrium line of the present BN phase diagram, where h-BN is a thermo-dynamically stable rather than the c-BN. Why would the present phase diagram of BN be not suitable for the synthesized methods mentioned above? It is well known that the size of critical nuclei is limited in several nanometer scales upon vapor-phase nucleation systems (such as ion-assisted CVD and PVD), the amount of grain boundaries in c-BN nanofilms is rather high, and therefore these materials should be called nanometer c-BN [2,13]. For the super-critical fluid synthesis, Horiuchi et al. had pointed out that the size of c-BN nuclei was in the range of 2–8 nm [11,12]. Consequently, the size effect on the formation of c-BN in the deep nanometer scale may be involved.

It is now known that the thermal properties, for example, the melting temperature, of all low-dimensional crystals depend on their size [14]. For free standing nanocrystals, the melting temperature decreases as its size reduces. For nanocrystals embedded in a matrix, they could melt below or above the melting point of the corresponding bulk crystal that is determined by the interface structure between embedded nanocrystals and the matrix [14,15]. If the interface is coherent or semi-coherent, there is an increase in the melting point. Otherwise, a depression of the melting point is present [16]. Some molecular dynamics simulations indicated that the free clusters exhibit a depression of the melting point with decreasing the size while embedded or coated clusters show superheating [15,17]. A thermodynamic calculation of size-dependent melting point was carried out by
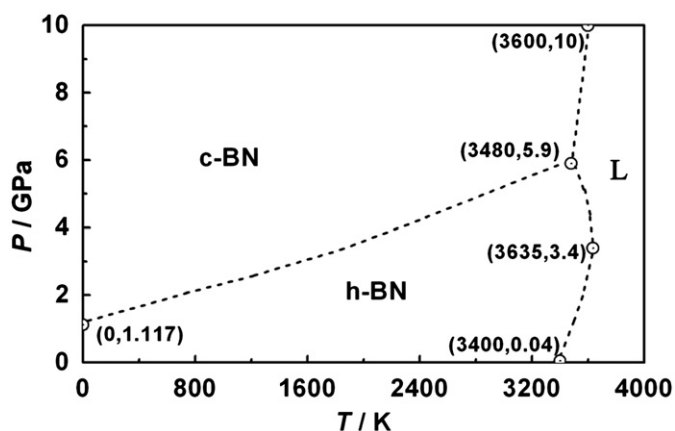
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Fig. 1. Last temperature–pressure phase diagram of bulk BN proposed by Solozhenko et al.

Pawlow and Hanszen, and then developed recently by Jiang et al. [14,18–20]. The developed thermodynamic model can predict the size-dependent melting point for various low-dimensional crystals. Furthermore, the thermodynamic theory can also explain the phase stability of solid nanocrystals by taking into account the size-dependence of the surface stress of nanocrystals [21]. Accordingly, herein we propose a thermodynamic method to establish the size-dependent phase diagram of BN. In particular, this developed phase diagram of BN can be used to predict the nanosized c-BN formation under the low-pressure synthesis methods, which might help us to exploit new techniques for the fabrication of c-BN nanomaterials.

2. Theory description

As for a nanostructure, it can be understood not only as the structure of a single nanoparticle, but also as a structure formed by a conglomerate of nanoparticles of any sizes [22]. A distinctive characteristic of a nanoparticle is the dependence of its properties on the particle size, which is recognized still in the classical theory of capillary by the Laplace–Young equation: $\Delta P = 4f/d$, where f denotes the surface stress and d is the particle diameter [22,23]. For the internal mechanical state of a nanoparticle, the surface stress of the first monolayer is important. Therefore, the surface stress could influence on phase transition in nanoparticles. However, due to its small size, a nanoparticle changes its phase state practically instantaneously so that it is hard to image the state of equilibrium between two phases inside the particle [22]. In this case, it is more reasonable to construct size-dependent BN phase diagram on the basis of its bulk phase transition boundaries.

Since the bulk BN phase diagram has been provided by previous researchers [4–10] (as shown in Fig. 1), the details of the bulk phase transition boundaries between h-BN and c-BN phase (denotation by hc), h-BN and liquid phase (denotation by hL), and c-BN and liquid phase (denotation by cL), respectively, can be obtained and showed in the following:

$$T_{hc}(\infty,P) = -812.703 + 727.577P \tag{1}$$

$$T_{hL}(\infty,P) = \begin{cases} 3397.202 + 69.94P \to 0.04 \leq P \leq 3.4 \\ 3845.8 - 62P \to 3.4 < P \leq 5.9 \end{cases} \tag{2}$$

$$T_{cL}(\infty,P) = 3307.32 + 29.268P \tag{3}$$

In order to distinguish from the nanosystem, the symbol of ∞ in the above equations denotes the bulk phase materials.

If a nanoparticle is subjected to external mechanical actions considered to be uniform along the nanoparticle surface for the sake of simplicity; the stable state of the nanoparticle must be not only related to the surrounding conditions, but also dependent on the surface stress [22]. For a spherical and isotropic BN nanocrystal with a diameter d, it must be subjected to the surrounding pressure P and an excess pressure ΔP created by surface stress in a solid particle. The total pressure P_t can be expressed as $P_t = \Delta P + P$. Accordingly, there are two extreme cases: one is $\Delta P \approx 0$, i.e. $P_t \approx P$ with $d \to \infty$, this case suggests the normal situation of pressure-dependent solid–solid phase transition for bulk materials; the other is $P \approx 0$, $P_t \approx \Delta P$, this case is the size-dependent solid–solid phase transition for nanosized materials [24]. Hereby, the equation of $P_t = \Delta P + P$ can be applicable for bulk and nanosized materials. Based on the bulk hc phase boundary shown in Eq. (1), the size-dependent transition temperature function T_{hc} can be expressed as

$$T_{hc}(d,P) = -812.703 + 727.577(P + 4f/d) \tag{4}$$

Here, f can be determined by $f = h[(S_{vib}H_m)/(2\kappa V_m R)]^{0.5}$ [25,26], where H_m is the bulk melting enthalpy of crystals, $S_{vib}(\infty)$ is the vibrational part of the total melt entropy $S_m(\infty)$, and $S_{vib}(\infty) \approx 0.19 S_m$ [26], κ is the compressibility, h is the atomic diameter and R is the ideal gas constant.

For bulk crystals, atoms in the surface layers can oscillate with large amplitude than atoms in the interior of the crystals, and the average amplitude of the whole crystal is independent on the size of the crystal [27]. However, it can be considered that in nanocrystals the atomic oscillation of large amplitude exists not only in the surface, but also in the core [27]. Thus, the melting behavior for the nanometer-size particles is expected to be size-dependent. To determine the melting temperature of h-BN, we use the Lindemann criterion, which says that a crystal will melt when the root mean-square displacement of the atoms in the crystal exceeds a certain fraction of the interatomic distance [24,27,28]. The Lindemann hypothesis is known to be valid qualitatively for nanoparticles [28,29]. Using both Lindemann criterion and Mott's equation for an isolated nanoparticle, the size-dependent melt temperature functions $T_m(d,P)$ of h-BN can be obtained as

$$T_m(d,P) = T_m(\infty,P)\exp\{-[2S_{vib}(\infty)/(3R)]/[d/(6h)-1]\} \tag{5}$$

Thus, the corresponding $T_{hL}(d,P)$ function is given as

$$T_{hL}(d,P)$$
$$= \begin{cases} (3397.202 + 69.94P)\exp\{-[2S_{vib}(\infty)/(3R)]/[d/(6h)-1]\} \to 0.04 \leq P(\text{GPa}) \leq 3.4 \\ (3845.8 - 62P)\exp\{-[2S_{vib}(\infty)/(3R)]/[d/(6h)-1]\} \to 3.4 < P(\text{GPa}) \leq 5.9 \end{cases}$$
$$\tag{6}$$

The triple point of h-BN, c-BN and liquid phase can be obtained when $T_{hL}(d,P)$ is equal to $T_{hc}(d,P)$ [24]. Therefore, the slope of the phase boundary between nanosized c-BN and liquid phase is expressed as

$$dT_{cL}(d,P)/dP = 29.268\exp\{-[2S_{vib}(\infty)/(3R)]/[d/(6h)-1]\} \tag{7}$$

As a result, the $T_{cL}(d,P)$ function is given as

$$T_{cL}(d,P) = T_t + 29.268\exp\{-[2S_{vib}(\infty)/(3R)]/[d/(6h)-1]\}(P-P_t) \tag{8}$$

3. Results and discussion

To plot the size-dependent phase diagram of BN, the parameters in Eqs. (4), (6) and (8) must be determined firstly. The value of h can be obtained on the basis of $h = \sqrt{3}a/4$ [25,26], where a is the lattice parameter. For c-BN, $a = 0.362$ nm, $S_m = 33.24$ J/(mol K); for h-BN, $a = 0.358$ nm, $S_m = 25$ J/(mol K) [7–10]. Since f of both c-BN and h-BN is the same on the equilibrium phase boundary, it can be