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Article

Thermodynamic Analysis about Nucleation and Growth of Cubic Boron Nitride Crystals in the hBN-Li_3N System under High Pressure and High Temperature †

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Abstract: The nucleation of cubic boron nitride (cBN) single crystals synthesized with lithium nitride (Li_3N) as a catalyst under high pressure and high temperature (HPHT) was analyzed. Many nanometer-sized cubic boron nitride nuclei formed in the near surface layer, as detected by high resolution transmission electron microscopy. Based on the experiment results, the transformation kinetics is described by a nucleation and growth process in the thermodynamic stability region of cBN. A theoretical description is developed based on the heterogeneous nucleation and layer growth mechanism, and the relevant parameters are estimated and discussed. The critical crystal radius, r^*, increases with the temperature under constant pressure; the change with temperature more pronounced at lower pressure (such as 4.5 GPa). The crystal growth velocity increased with the temperature, and it is parabolic with temperature under certain pressure. These results are consistent with experimental data.

Keywords: cubic boron nitride; high pressure and high temperature; critical nucleation radius; crystal growth velocity

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1. Introduction

Cubic boron nitride single crystals, as a functional material, have many interesting properties, such as high thermal conductivity, high hardness second only to diamond and excellent chemical stability. Furthermore, they are typical III-V group semiconductor materials with a wide energy gap, which can easily be made into both p- and n-type with suitable impurity additions [1–3]. At present, cBN single crystals can be synthesized by various methods, among which the static catalyst synthetic method under HPHT is commonly used [4,5]. According to this method, hexagonal boron nitride (hBN) is the source for boron and nitrogen. Meanwhile, in order to decrease the synthetic temperature and pressure, many catalysts including alkali and alkaline earth nitrides, ammonium salts, and even water are proposed for HPHT synthesis of cBN crystals [6,7].

The high pressure and temperature required make obtaining large cBN crystals difficult; furthermore, the necessary conditions for such synthesis have not been well delineated [8]. Due to the differences in equipment and synthesis methods, researchers may draw the different conclusions from their experimental results. Against this background, some work has been undertaken to investigate the kinetics of the phase transition and discuss the mechanism about nucleation and crystal growth. A first version of a *P*, *T*-diagram for boron nitride was proposed by Bundy and Wentorf [9] in 1963 based on experimental data, and the conversion from hexagonal to cubic form under HPHT conditions was depicted in detail. Fukunaga [10] determined the phase boundary between hexagonal and cubic boron nitride by careful observation of the transformation behavior. However, the mechanism of nucleation and crystal growth is still a subject for discussion, especially by thermodynamic analysis.

In this paper, critical crystal radius and crystal growth velocity of cBN under different pressure and temperature are calculated from existing thermodynamic data. Combined with the related experiments results, the mechanism of nucleation and crystal growth are also discussed.

2. Experiments and Calculation

2.1. Experiments Section

The cBN crystals were synthesized by a static HPHT method. As starting materials, the hBN (purity 99.9%) was well-mixed with Li_3N as catalyst in a cubic anvil with the weight ratio of 9:1 and with pyrophyllite as the pressure transmitting medium. The cell assembly was brought up to a pressure of 4.6–4.8 GPa by the high pressure apparatus and then heated to a temperature of approximately 1850 K. After keeping the sample at this temperature for 10 min, the temperature was decreased rapidly by turning off the electric power, and the synthesized samples were quenched from high temperature to room temperature and the high pressure was decreased to ambient pressure.

The fracture morphology of synthesized sample was examined with a JSM-6380LA (JEOL Ltd, Akishima, Japan) type scanning electron microscope (SEM). The powder in the near-surface region which surround the cBN crystal matrix were carefully collected under the view of an optic microscope,

and their phases were determined by means of a JEM-2010F (JEOL Ltd, Akishima, Japan) type high resolution transmission electron microscope (HRTEM) with an operating voltage of 200 kV.

2.2. Calculations

The cBN can be synthesized under HPHT conditions, and this process could be explained by the kinetics of nucleation and growth. The critical crystal radius, r^*, is the essential parameter for crystal nucleation, and the linear growth velocity, v, is independent of time for interface-controlled growth.

According to classical theory of nucleation [11], in the processing of transformation from hBN to cBN, the Gibbs free energy difference, $\Delta G(r)$, which includes volume free energy difference and surface free energy difference, is given by:

$$\Delta G(r) = (\frac{4}{3}\pi r^3 \bullet \frac{\Delta G_V}{V_m} + \frac{20}{3}\pi r^2 \sigma_{Ls})(\frac{2-3\cos\theta+\cos^3\theta}{4}) \tag{1}$$

Here r stands for nucleus radius, ΔG_V is molar volume free energy difference and V_m is molar volume of cBN. θ is contact angle between mold wall and crystal nucleus which are formed under HPHT with spherical cap shape, and σ_{Ls} represents surface tension coefficient.

ΔV, which represents molar volume difference between hBN and cBN, is described by:

$$(\frac{\partial \Delta G_V}{\partial P})_r = \Delta V \tag{2}$$

when temperature is a constant, ΔG_V can be expressed as Equation (3) with pressure increases from P_0 to P,

$$\Delta G_V(P) - \Delta G_V(P_0) = \Delta V(P - P_0) \tag{3}$$

According to Fukunaga [10], the P-T balancing line between hBN and cBN is given by Equation (4):

$$P_0(\text{GPa}) = \frac{T(^\circ\text{C})}{465} + 0.79 \tag{4}$$

when $\Delta G(r)$ reaches the maximum, which means $\partial \Delta G(r)/\partial r = 0$, at this point, the critical crystal radius, r^*, could be calculated as follows:

$$\frac{\partial \Delta G(r)}{\partial r} = (4\pi r^2 \bullet \frac{\Delta G_V}{V_m} + \frac{40}{3}\pi r \sigma_{Ls})(\frac{2-3\cos\theta+\cos^3\theta}{4}) = 0 \tag{5}$$

For a certain system, θ is a constant, so Equation (5) means:

$$4\pi r^{*2} \bullet \frac{\Delta G_V}{V_m} + \frac{40}{3}\pi r \sigma_{Ls} = 0 \tag{6}$$

According to Equations (3) and (4), the critical crystal radius, r^*, is given by:

$$r^* = -\frac{10\sigma_{Ls}V_m}{3\Delta G_V} = -\frac{10\sigma_{Ls}V_m}{3\Delta V[P - T/465 - 0.79]} \tag{7}$$

From Equation (7), the critical crystal radii are calculated at different pressures and temperatures [12].

According to classical theory of nucleation, the growth velocity, v, is given by reference [13]:

$$v = C_G \exp(-\frac{E_D}{kT})(\frac{\Delta\mu}{kT})^{\frac{5}{6}} \exp(-\frac{\pi\gamma^2}{\Delta\mu kT}) \quad (8)$$

where C_G is a temperature independent constant, E_D is the activation energy for diffusion and γ represents edge free energy of the two-dimensional nucleus. Δμ is the difference of the free enthalpies of both phases and is expanded around the equilibrium point (P_0, T_0):

$$\Delta\mu = (P - P_0)\Delta V_0 + (1 - T/T_0)\Delta h_0 \quad (9)$$

Here Δh_0 and ΔV_0 stand for heat of transition and volume change, respectively, in the point (P_0, T_0). When the pressure is constant ($P = P_0$), Δμ is proportional to the (T_0-T). γ represents the interface free energy between crystal and melt. The temperature dependence of γ is less essential and can be regarded as constant because in the nucleation process there is no roughening transition.

The activation energy for diffusion, E_D, is described as:

$$E_D(P) = E_D(P_0) + V_A(P - P_0) \quad (10)$$

When $P = P_0$:

$$\Delta\mu = (1 - T/T_0)\Delta h_0, \ \Delta h_0 = 0.7kT_0 \quad (11)$$

By above calculating method, the growth velocity at different pressures and temperatures was calculated.

3. Results and Discussion

Figure 1 shows the growth step on the cBN crystal surface, and this implies growth initiates by two-dimensional nucleation. The structures and morphologies of the near-surface region in cBN are closely associated with the crystal growth under HPHT, and it may be of great significance to explain the process of cBN growth [14,15]. When the synthetic process was finished and the synthetic cell assembly was cooled rapidly, much information about cBN growth under HPHT could be recorded.

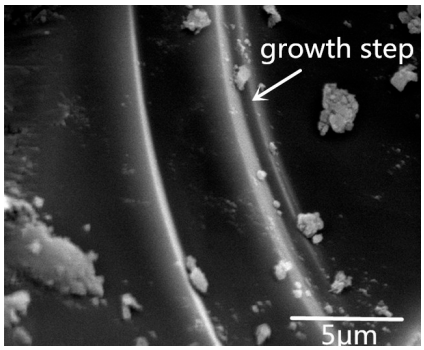

Figure 1. The growth step of cBN crystal.

Figure 2 shows the HRTEM image of sample collected from the near-surface region of cBN crystals surface. According to the two dimension lattice stripe photograph, the phase in selected area is inferred as nanometer-sized cBN nucleus with a reflection of g = 110. Those particles have no obvious crystal shape and cannot be distinguished by optical microscope, and they are distributed all over the sample.

These nanometer-sized cBN nuclei could be transformed from hBN with catalysis of Li_3BN_2, and its size and growth velocity are closely related to synthesized pressure and temperature.

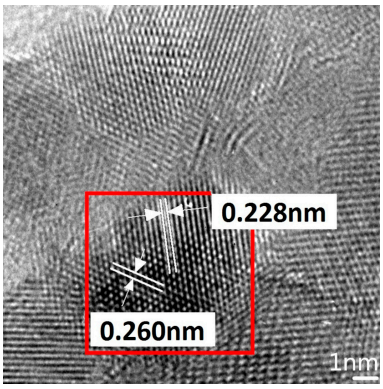

Figure 2. HRTEM image of cBN particle in the near-surface region of cBN crystal.

Figure 3 shows the influence of temperature on the critical crystal radius under different pressure. When pressure is constant, the critical crystal radius increases with the increase of temperature. At lower pressure (such as P = 4.5 GPa shown in Figure 3), the crystal radii is strongly dependent on temperature, more than doubling with a 150 degree temperature increase. In contrast, at high pressure (P = 6.0 GPa), the temperature dependence of the nucleation radii is much weaker, doubling only after a 500 degree temperature change. Similarly, the critical crystal radii are decreasing with the higher pressure when the temperature remains unchanged, and this changing trend is obvious under lower pressure. The calculated results show the cBN crystals would have larger critical radii under lower pressure and at higher temperature, and cBN crystals with coarse grain structure could be obtained under these conditions.

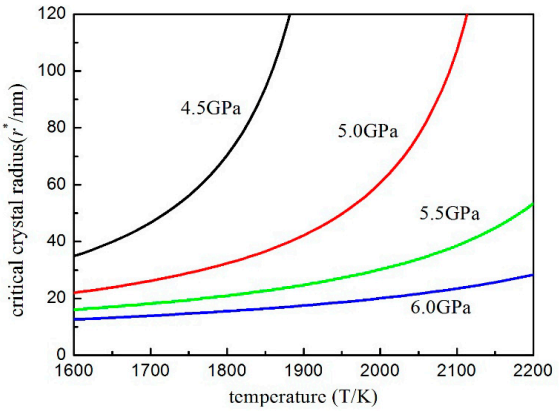

Figure 3. The relationship between critical crystal radius r^* and temperature under different pressures.

From the above results, it can be inferred that the critical radii are closely related to synthesis pressure and temperature. The coarse crystals could be obtained under lower pressure and higher temperature, for the critical radius depends more on temperature under lower pressure. However, the larger critical radii may make the phase transition probability decreased, and makes the nucleation

more difficult. This result is consistent with our experiments, and crystals which are synthesized under lower pressure and lower temperature are of poor quality in reality.

Figure 4 shows the relationships between crystal growth velocity and temperature under different pressures. According to synthesized experiments, we limit the temperature scope is 1600–2200 K, and the pressure scope is 4.5–6.0 GPa. The growth velocity exhibits parabolic trend with the increasing temperature under different pressures. At lower temperature, the crystal growth velocities changes slightly with pressures, but it can be influenced obviously with the increase of temperature. At 5.5 GPa, the growth velocity of cBN crystals has maximum value compared to other pressures. For the phases have short and medium range orders under HPHT conditions, so they could exist with certain flowability. Once the nanometer-sized cBN nuclei were formed in the HPHT melt, it could diffuse towards to larger crystal nuclei to decrease the free energy of system. The whole diffusion velocity is controlled by the synthesized pressure and temperature. When the pressure gets higher, the activation energy of diffusion gets higher, so the diffusion velocity gets slower. On the other hand, the diffusion coefficient gets higher with the increasing of temperature. Considering the effect of pressure and temperature, the cBN has smaller nucleation radius and lower nucleation energy under 5.5 GPa pressure, and the nucleation process would become easier. The diffusing process becomes easier with the concentration of cBN particles gradually become higher, so the cBN crystals would have the higher growth velocity under this condition.

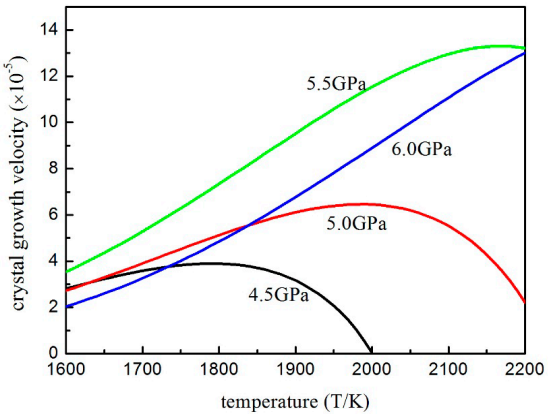

Figure 4. The relationships between crystal growth velocity and temperature under different pressures.

According to our earlier works [16,17], during cBN crystal growth under HPHT, Li_3N first reacts with hBN to produce Li_3BN_2, and the cBN could be directly transformed from hBN with the catalyst of Li_3BN_2. The possible mode of catalyzing hBN to cBN is closely related to the Li_3BN_2 for its existence in the interface. Li_3BN_2 has short-range ordered under HTHP, and it can be dissolved into well-ordered hBN [18]. Without a catalyst, a temperature higher than 3000 K and pressure higher than 13 GPa are needed to obtain cBN single crystal [19]. The role of catalyst is to promote nucleation and to reduce the corresponding activation enthalpy.

4. Conclusions

In this paper, the cBN crystals were synthesized by Li_3N as catalyst under HPHT conditions, and nanometer-sized cBN nuclei are found near the surface of cBN crystals. The experimental results are well described by the classical theory of nucleation and growth. From the systematic investigation on the nucleation and growth velocity in the cBN synthesis under HPHT conditions, the critical radii are clearly influenced by temperature and pressure. When the pressure is constant, with the increase of temperature, the critical crystal radius is increasing, and it has a gentle tendency to increase under higher pressure. On the other hand, when the temperature is constant, critical crystal radius is increasing with the pressure gets higher, and pressure has a main influence on the nucleation when the temperatures above a certain threshold. Also, the growth velocity increases parabolically with temperature at constant pressure. Under 5.5 GPa, the growth velocity is higher than other pressures. The role of catalyst is to promote nucleation and to reduce the corresponding activation enthalpy. From these results, it could be deduced that coarse cBN crystals would be obtained under lower pressure and higher pressure for its higher critical crystal radius, but this process has a lower phase transition probability, so considering the growth velocity and critical crystal radius, the moderate size cBN crystals with high quality should be synthesized under medium pressure and temperature in actual production.

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Author Contributions

Bin Xu conceived of the ideal that we can apply thermodynamic method to analysis the crystal growth under HPHT conditions. His main contribution is the problem motivation. Xiao-fei Guo established the structure scheme of thermodynamic model and made substantial contributions to conception and design of this paper. Xiao-fei Guo, Bin Xu, Wen Zhang, and Hong-Mei Yang performed acquisition, analysis, and interpretation of data. Xiao-fei Guo and Bin Xu drafted the paper. Mei-zhe Lv and Xiao-hong Fan participated in analysis and interpretation of data, and gave useful suggestions for revising the manuscript; Bin Xu gave final approval of the version to be submitted and any revised version. All authors have read and approved the final manuscript.

Conflicts of Interest

The article has been written by the stated authors who are all aware of its content and approve its submission, no conflict of interest exists.

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