



Thermodynamic Analysis About Nucleation and Growth of Cubic Boron Nitride in the System BN-Li₃N Under High Pressure and High Temperature

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Abstract: In this paper, cubic boron nitride (cBN) single crystals are synthesized with lithium nitride (Li₃N) as catalyst under high pressure and high temperature (HPHT). A lot of nanometer-sized cubic boron nitride nucleuses are found in the near surface layer of cBN crystals by high resolution transmission electron microscopy examinations. Based on the experiment results, the transformation kinetics is described by a nucleation and growth process in the thermodynamic stability region of cBN. The theoretical description is based on the heterogeneous nucleation and layer growth mechanism, and the relevant parameters are estimated and discussed. The results show that critical crystal radius, r^* , is increasing with the elevated temperature under the same pressure, and temperature is the main influence on it under lower pressure. At the same time, the results show that crystal growth velocity has different changing tendency with different pressure under proper synthesized scope. The effect of the catalyst is suggested to lower the activation enthalpy for nucleation. These results are well consistent with experimental data.

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

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1. Introduction

Cubic boron nitride single crystal, as a functional material, has many interesting properties, such as thermal conductivity, high hardness only second to diamond and excellent chemical stability. Furthermore, they are typical III-V group semiconductor materials with a wide energy gap, which can be made easily 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 that method, hexagonal boron nitride (hBN) is used as boron and nitride element sources. Meanwhile, in order to decrease the synthetic temperature and pressure, many catalysts including alkali and alkaline earth nitrides, ammonium salts, and even water were proposed for HPHT synthesis of cBN crystals [6, 7].

It may be understood that the key problem in obtaining large crystals of high quality is to control the synthesized pressure and temperature, but the general regulation about synthesized conditions to obtain a well-faceted large single crystal has not been successfully established [8]. For the difference of equipments and synthesized methods, researchers maybe draw the different conclusions through their experiments results. On the basis of this background, some work was undertaken to investigate the kinetics of the phase transition and to discuss the mechanism of nucleation and crystal growth. A first version of p , T -diagram for boron nitride was proposed by Bundy and Wentorf [9] in 1963 based on experimental data, and the conversion from hBN into the cubic form under HPHT conditions was depicted in details. Fukunaga had determined the phase boundary between hexagonal and cubic boron nitride by careful observation of the transformation behavior [10]. However, the mechanism of nucleation and crystal growth is still a subject for discussion, especially by the thermodynamic calculation as methods.

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

2. Experiments and calculation

2.1 experiments section

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

decrease 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 the ambient pressure.

The morphology of synthesized sample was examined with JSM-6380LA type SEM. The near-surface region samples were carefully collected from the cBN crystal matrix under the view of an optic microscope, and their phases were determined by means of JEOL JEM-2010F type HRTEM with an operating voltage of 200kV.

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 the 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

$$\Delta G(r) = \left(\frac{4}{3} \pi r^3 \cdot \frac{\Delta G_v}{V_m} + \frac{20}{3} \pi r^2 \sigma_{L_s} \right) \left(\frac{2 - 3 \cos \theta + \cos^3 \theta}{4} \right) \quad (1)$$

Where r is nucleus radius, ΔG_v is the molar volume free energy difference and V_m is the molar volume of cBN. θ is the contact angle between mold wall and crystal nucleus which formed under HPHT with spherical cap shape, and σ_{L_s} represents the surface tension coefficient.

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

$$\left(\frac{\partial \Delta G_v}{\partial P} \right)_r = \Delta V \quad (2)$$

When temperature is constant, ΔG_v can be expressed as Eq. 3 with pressure increases from P_0 to P ,

$$\Delta G_v(P) - \Delta G_v(P_0) = \Delta V(P - P_0) \quad (3)$$

According to reference [10], the P - T balancing line between hBN and cBN is given by

$$P_0 = \frac{T + 273}{465} + 0.79 \quad (4)$$

When $\Delta G(r)$ reach the maximum, that means $(\partial \Delta G(r) / \partial P)_r = 0$, the critical crystal radius, r^* , is given by

$$r^* = - \frac{10 \sigma_{L_s} V_m}{3 \Delta G_v} = - \frac{10 \sigma_{L_s} V_m}{3 \Delta V [P - (T - 273) / 465 - 0.79]} \quad (5)$$

From Eq. 5, the critical crystal radius could be calculated with different pressure and temperature [12].

Fig. 1 shows the growth step on the cBN crystal surface, and this means the growth pattern of cBN is two-dimension nucleation. According to the classical theory of nucleation, the growth velocity, v , is given by [13]

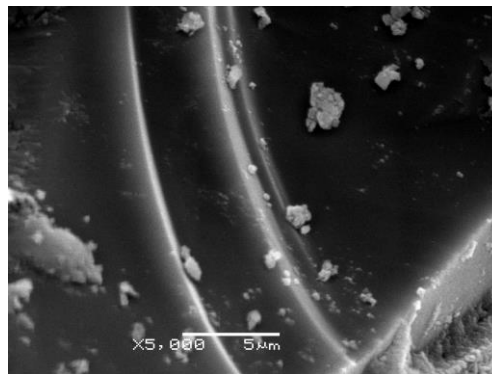
$$v = C_G \exp\left(-\frac{E_D}{kT}\right) \left(\frac{\Delta\mu}{kT}\right)^{\frac{5}{6}} \exp\left(-\frac{\pi\gamma^2}{\Delta\mu kT}\right) \quad (6)$$

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. $\Delta\mu$ is the difference of the free enthalpies of both phases and is expanded around the equilibrium point (P_0, T_0)

$$\Delta\mu = (P - P_0)\Delta V_0 + (1 - T/T_0)\Delta h_0 \quad (7)$$

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

Figure 1. The growth step of cBN crystal



The activation energy for diffusion, E_D , is described as

$$E_D(P) = E_D(P_0) + V_A(P - P_0) \quad (8)$$

When the $P=P_0$,

$$\Delta\mu = (1 - T/T_0)\Delta h_0, \quad \Delta h_0 = 0.7kT_0 \quad (9)$$

By above method, the growth velocity under different pressure and temperature could be calculated.

3. Results and Discussion

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 finished and the synthetic cell assembly was cooled rapidly, much information about cBN growth under HPHT could be recorded.

Fig. 2 shows the HRTEM image of sample which collected from the near-surface region of cBN crystals. 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 nucleuses could be transformed by 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

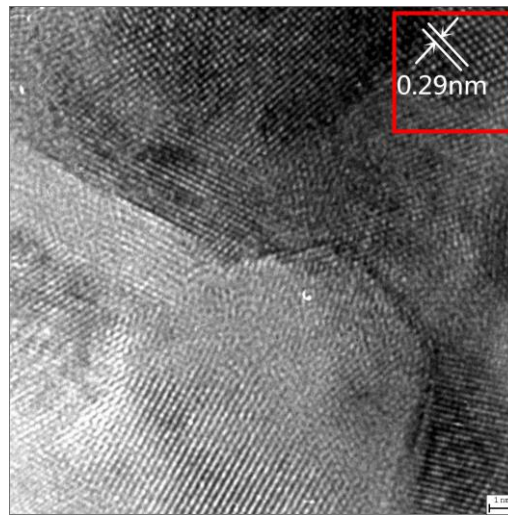
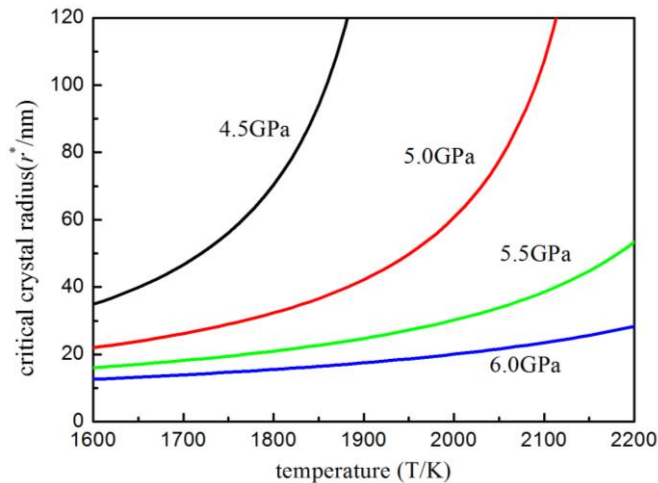


Fig. 3 shows the influence of different temperatures to critical crystal radius under different pressure. When the pressure is constant, with the increase of temperature, the critical crystal radius is increasing. Under lower pressure (such as $P=4.5\text{GPa}$ shown as Fig. 3), the critical crystal radius increases rapidly, so the temperature is the main affecting factor in this nucleation process. However, under high pressure (such as $P=6.0\text{GPa}$ shown as Fig. 3), the critical crystal radius has a tendency to increase, but the tendency is not obvious, and it means temperature has little influence on the nucleation of cBN under high pressure. Similarly, the critical crystal radius is increasing with the higher of pressure when the temperature is constant, and this changing trend is obvious under low pressure. The calculated results show the cBN crystals would have larger critical radius under lower pressure and at higher temperature, and cBN crystals with coarse grain structure could be obtained under these conditions.

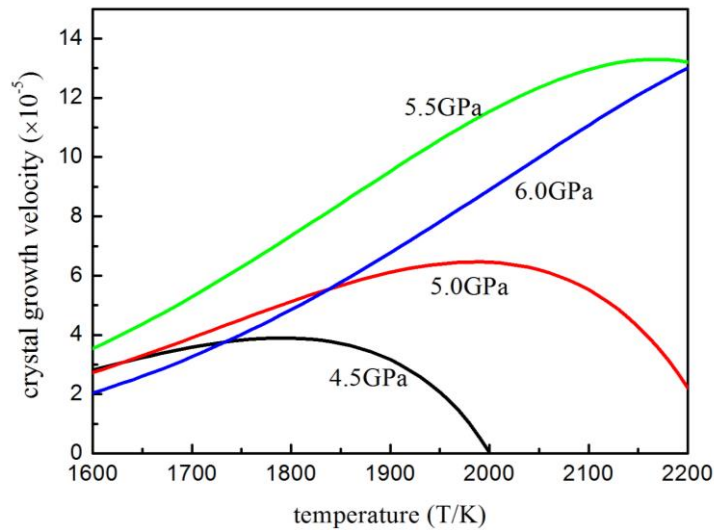
Figure 3. The relationships between critical crystal radius r^* and temperature under different pressures



From above results, it can be inferred that the critical radius is closely related to synthesized 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 radius maybe makes the phase transition probability decreased, and makes the nucleation more difficult. This result is consistent to our synthesized experiments, and the crystals which are synthesized under lower pressure and lower temperature have poor quality in reality.

Fig. 4 shows the relationships between crystal growth velocity and temperature under different pressures. According to the previous synthesized experiments, we limit the temperature scope is 1600-2200K, and the pressure scope is 4.5-6.0GPa. It can be obviously observed that growth velocity exhibits parabolic trend with the increasing temperature under different pressures. At lower temperature, the crystal growth velocities with different pressures change a little, but it can be influenced obviously with the increasing of temperature. When the synthesized pressure reaches to 5.5GPa, the growth velocity of cBN crystals has the maximum 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 nucleuses were formed in the HPHT melt, it could diffuse towards to the larger crystal nucleuses 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 5.5GPa pressure, and the nucleation process would become easier. The diffusing process gets 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 should be first react with hBN to produce Li_3BN_2 , and the cBN could be transformed hBN directly. 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 is short-range ordered under HTHP, and it can be dissolved into well-ordered hBN [18]. Without catalyst, higher temperature than 3000K and higher pressure than 13GPa are needed to obtain cBN crystal [19]. It could be explained that the role of catalyst is to consist in the promotion of nucleation and to reduce the corresponding activation enthalpy by above thermodynamic calculations.

4. Conclusions

In this paper, the cBN crystals are synthesized by Li_3N as catalyst under HPHT conditions, and the nanometer-sized cBN nucleuses are found in the near surface region. 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, it is found that critical crystal radius is influenced by temperature and pressure obviously. 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 the main influence on the nucleation when the temperatures above a certain threshold.

Also, it can be obvious observed that growth velocity exhibits parabolic trend with the increasing temperature under different pressures. Under 5.5GPa, the growth velocity is higher than other pressure.

As to the role of catalyst, it could be explained to consist in the promotion of nucleation and to reduce the corresponding activation enthalpy.

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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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