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THE INFLUENCE OF COMPRESSIVE STRESS ON THE FORMATION OF CUBIC BORON NITRIDE THIN FILM*

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The elastic strain energy and Gibbs free energy of cubic BN (cBN) thin film in biaxial stress field are calculated. The results show that the stress in cBN thin films has an impact on the formation of cubic phase. It is concluded that the high compressive stress in the cBN thin films is not the cause of cBN formation. This conclusion is different from that predicted by compressive stress model; however, it could well account for the experimental results. At a given substrate temperature, there is a compressive stress threshold, below which cBN phase is thermodynamically stable and above which hexagonal BN(hBN) phase is thermodynamically stable. At room temperature the compressive stress threshold is calculated to be 9.5 GPa.

PACC: 6840; 6890

I. INTRODUCTION

Cubic boron nitride (cBN) thin film has been received considerable attention because of its excellent physical and chemical properties, which are comparable to those of diamond. Just like diamond cBN has low density, high hardness, high chemical stability, wide band gap(> 6.4V), and large thermal conductivity. Furthermore, cBN is superior to diamond in the application for cutting tools due to its chemical stability and without any interaction with ferrous elements during machining ferrous materials. Diamond is limited for the purpose of cutting tools because of its reaction with ferrous elements. As a semiconductor material, cBN can be easily doped as n-or p-type and has a very high beakdown voltage. Therefore, cBN is a promising wide-band gap III-V semiconductor suitable for high power transistor and optoelectronic devices.

Many methods for preparing cBN films have been reported including physical vapor deposition and chemical vapor deposition. Recently it is widely accepted that the impact of energetic ions is a key issue for the growth of cBN films.[1] The cBN films synthesized by energetic ions have very high compressive stress. It has not been determined whether the cBN formation is a cause or result of the high compressive stress[2,3], although Mckenzie *et al.* regarded the formation of cBN as a result of compressive stress action.[4]

In this paper we have calculated the Gibbs free energy of cBN film in biaxial stress field as a function of biaxial stress and substrate temperature. Based on the calculated results, the influence of compressive stress on the formation of cBN thin films is discussed. The calculation can well account for some experimental results.

II. CALCULATION OF GIBBS FREE ENERGY OF cBN THIN FILM

A. The substrate at room temperature

In BN films with a high cBN content deposited by ion- or plasma-assisted methods, a layered structure is typically produced. This structure consists of an amorphous layer at the substrate-film interface, a near interfacial region of hexagonal boron nitride (hBN), a layer consisting primarily of small and highly defective crystallites of cBN, and a final thin layer of hBN.[5] In the hBN layer the *c*-axis is in the plane of the film,[6] and the [111] direction is also in the plane of the film.[7] The cBN formation occurs below the film surface where hBN is transformed to cBN.[2]

Usually, the common assumption in the literature about film stress is that a film is in a state of pure biaxial stress ($\sigma_{11} = \sigma_{22} = \sigma$, all other $\sigma_{ij} = 0$).[8] Now we assume that in thin BN films the hBN is transformed to cBN under the action of a biaxial compressive stress, and the stress plane is parallel to the substrate. The stress arises from energetic particles acting on the film material has sufficient strength to sustain stress without plastic deformation.[4]

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The expression for the Gibbs free energy in a general stress field is[4,9]

$$G(T,\sigma_{ij}) = U - TS - v\sum_{ij}\varepsilon_{ij}\sigma_{ij}, \tag{1}$$

where U and S are the internal energy and entropy, respectively, ε and σ are the strain and stress tensors, respectively, v is the volume. From Eq.(1) we obtain

$$\begin{aligned} G(T,\sigma_{ij}) &= G(T,0) - v\sum_{ij}\int_0^{\sigma}\varepsilon_{ij}\mathrm{d}\sigma'_{ij} \\ &= G(T,0) - v\sum_{\substack{ij\\kl}}\int_0^{\sigma} s_{ijkl}\sigma'_{kl}\mathrm{d}\sigma'_{ij} \\ &= G(T,0) - vw, \end{aligned} \tag{2}$$

where s_{ijkl} is compliance coefficients, w is the strain energy per unit volume. The expression for w is written as[10]

$$w = \frac{1}{2}\sigma'_{ij}\varepsilon'_{ij} = \frac{1}{2}s_{ijkl}\sigma'_{ij}\sigma'_{kl}. \tag{3}$$

If we consider the stress field as a biaxial stress field, for cBN [111] axis lying in the stress plane, then Eq.(3) can be expressed as

$$w = \frac{1}{8}\sigma^2(6s^{\mathrm{c}}_{11} + 10s^{\mathrm{c}}_{12} + s^{\mathrm{c}}_{44}); \tag{4}$$

for hBN c-axis lying in the stress plane, Eq.(3) can be written as

$$w = \frac{1}{2}\sigma^2(s^{\mathrm{h}}_{11} + s^{\mathrm{h}}_{33} + 2s^{\mathrm{h}}_{13}). \tag{5}$$

From Eqs.(2),(4) and (5), the Gibbs free energies for cBN and hBN can be obtained, respectively,

$$G_{\mathrm{c}}(T,\sigma) = G(T,0) - \frac{1}{8}\sigma^2(6s^{\mathrm{c}}_{11} + 10s^{\mathrm{c}}_{12} + s^{\mathrm{c}}_{44})v_{\mathrm{c}}, \tag{6}$$

$$G_{\mathrm{h}}(T,\sigma) = G(T,0) - \frac{1}{2}\sigma^2(s^{\mathrm{h}}_{11} + s^{\mathrm{h}}_{33} + 2s^{\mathrm{h}}_{13})v_{\mathrm{h}}. \tag{7}$$

By using the data presented in Table 1, we can calculate the Gibbs free energy of cBN and hBN for a definite σ. Suppose $T = 298.15$K and G_{h}(298.15K,0)=0, then G_{c}(298.15K,0)=ΔG(298.15K,0), and the Gibbs free energy from Eqs.(6), (7) is illustrated in Fig. 1.

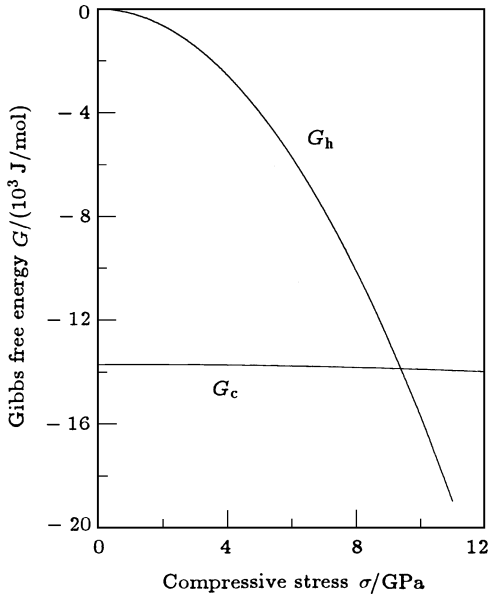


Fig.1. Gibs free energy of cBN and hBN for different compressive stresses at room temperature.

Table 1. Related data used for calculation of Gibbs free energy.

Parameters	Value	Source
c^{h}_{11}	830 GPa	Ref.[11]
c^{h}_{12}	130 GPa	Ref.[11]
c^{h}_{33}	35.6 GPa	Ref.[11]
c^{h}_{13}	12.5 GPa	Ref.[10]
c^{c}_{11}	831 GPa	Ref.[12]
c^{c}_{12}	420 GPa	Ref.[12]
c^{c}_{44}	450 GPa	Ref.[12]
s^{h}_{11}	1.24× 10^{-3}/GPa	calculated from c_{ij}
s^{h}_{13}	-3.69× 10^{-4}/GPa	calculated from c_{ij}
s^{h}_{33}	2.83× 10^{-2}/GPa	calculated from c_{ij}
s^{c}_{11}	1.82× 10^{-3}/GPa	calculated from c_{ij}
s^{c}_{12}	-6.12× 10^{-4}/GPa	calculated from c_{ij}
s^{c}_{44}	2.22× 10^{-3}/GPa	calculated from c_{ij}
ΔG(298.15K,0)	-13.7kJ/mol	Ref. [13]
v_{h}	10.892 cm^3/mol	Ref.[14]
v_{c}	7.113 cm^3/mol	Ref.[15]

B. $\Delta G = G_c - G_h$ varying with the compressive stress and substrate temperature

By using the values of compliance coefficients given in Table 1, the thermal expansion coefficients, and the heat capacity of BN,[14,16,17] the values of $\Delta G = G_c - G_h$ are calculated by the following equation,[9] and the results are illustrated in Fig. 2.

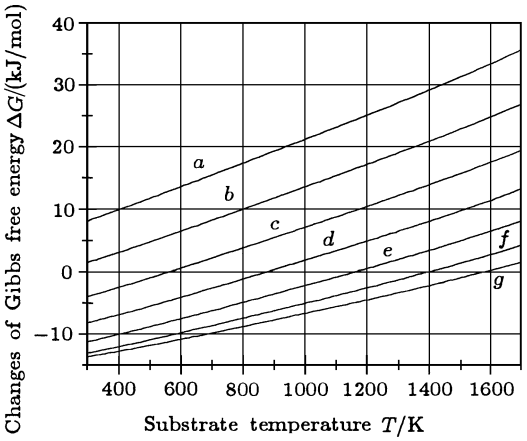


Fig.2. Changes of $\Delta G = G_c - G_h$ with compressive stress and temperature. For curves a, b, c, d, e, f and g, σ is 12, 10, 8, 6, 4, 2 and 0 GPa, respectively.

$$dG(\sigma_{ij}, T) = -\varepsilon_{ij} d\sigma_{ij} - S dT, \quad (8)$$

$$d\varepsilon_{ij} = s_{ijkl} d\sigma_{kl} + \alpha_{ij} dT, \quad (9)$$

$$dS = \alpha_{ij} d\sigma_{ij} + (C/T) dT, \quad (10)$$

where G is Gibbs free energy, T is the absolute temperature of the substrate and thin films, α is the thermal expansion coefficient tensor, C is heat capacity, S is entropy, ε and σ are the strain and stress tensors, respectively, and s is compliance coefficient.

From Figs.1 and 2, the values of T and σ at which $\Delta G = 0$ can be obtained, which are listed in Table 2.

Table 2. The values of T and σ at which ΔG=0.

$\Delta G = G_c - G_h$	0	0	0	0	0
σ/GPa	9.5	8	6	4	2
T/K	298	560	880	1160	1400

Ⅲ. DISCUSSION

A. Thermodynamic state of cBN in BN films at different compressive stresses

Figure1 illustrates the Gibbs free energies of cBN and hBN at room temperature (T=298K) under different compressive stresses. It is obvious that $G_h > G_c$ when $\sigma > 9.5$GPa, $G_h < G_c$ when $\sigma > 9.5$ GPa, and $G_h = G_c$ when $\sigma = 9.5$GPa. Therefore, cBN is a thermodynamically stable phase when $\sigma < 9.5$GPa, and hBN is thermodynamically stable phase when $\sigma > 9.5$ GPa, and $\sigma = 9.5$GPa is the point at which cBN and hBN are in thermodynamical equilibrium. Then 9.5GPa is the stress threshold at room temperature, below which cBN is the thermodynamically stable phase in BN films. Based on this conclusion, it is deduced that cBN, is a thermodynamically stable phase at standard conditions, not hBN. Similar phenomenon was observed by Sachdev *et al.*[18] during their investigations on the cBN/hBN phase transformation.

From the phase transformation theory, we know that the phase transformation from hBN to cBN can occur more easily when the two phases have the same Gibbs free energy. In this case no potential barriers need to overcome. Therefore, the BN film that contains the highest cBN content can be obtained. At room temperature, the value of stress threshhold is 9.5 GPa.

The threshold values of compressive stress at the thermodynamic equilibrium points ($\Delta G = G_c - G_h = 0$) of cBN and hBN vary with the substrate temperature,as shown in Fig.2 and Table 2. When $\sigma \geq 10$GPa, at any temperature, $\Delta G = G_c - G_h$ always > 0, there are no thermodynamic equilibrium points. When $\sigma <$ 10 GPa, the threshold value of compressive stress at the thermodynamic equilibrium point decreases with increasing substrate temperature. Therefore, the compressive stress at which the film contains the highest cBN content decreases with increasing temperature.

Our calculations also indicate that cBN can be formed at very low compressive stress when the substrate temperature is high enough, because cBN has lower Gibbs free energy than hBN.

B. Comparison with experimental results

Some experimental results about the threshold value of compressive stress in cBN films are shown in Fig. 3.[3,19,20] In each curve of $a - d$, there is a critical σ at which the film has the highest cBN content. The critical σ point may be the thermodynamic equilibrium point of cBN and hBN phases, as discussed above. For different curves $a - c$, the critical σ point is different (4.0, 8.8 and 10.5GPa).This may be due to the different substrate temperatures for the formation of BN films. If this is true, the results are in good agreement with our calculated results. For curve d,

the critical σ point is at 17GPa; however, according to our calculation, at $\sigma = 17$GPa, there is no thermodynamic equilibrium point of cBN and hBN for any temperatures, so there should be no point corresponding to the highest cBN content. During the calculation we assume the films are under elastic strain. Curve d is not in agreemnt with our calculation, this may be due to plastic deformation as described in the paper.[5]

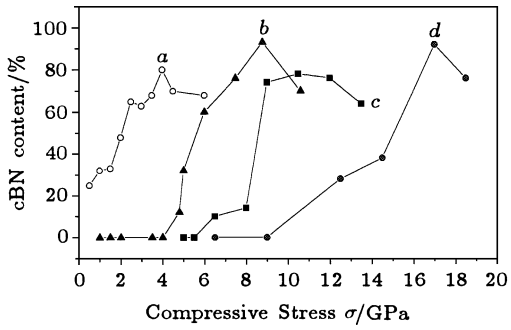


Fig.3. Relationships between film stress and cBN content. Curves a, b, c and d are reproduced from Refs.[19],[3],[20], respectively.

Cardinale *et al.*[3] and Reinke *et al.*[21] have shown that if cBN and hBN have the same ion-induced strain, cBN will have a much higher stress because of its higher elastic modulus. That is, since the effective modulus of the film increases with increasing cBN content, the stress will necessarily increase. This is the reason why the film stress (Fig.3) increases with increasing cBN content. Furthermore, according to our calculation, cBN is the thermodynamically stable state at very low compressive stress. Based on the above facts, it can be concluded that the high compressive stress of the cBN films results from the formation of cBN films rather than results in cBN formation.

C. Discussion about compressive stress model

The ion bombardment that is critical to cBN synthesis also generates significant compressive stresses in the films.[3] In 1991, McKenzie *et al.*[6] proposed a compressive stress model for cBN formation, in which the cBN phase is suggested to be formed under the action of the ion-induced stress, i.e., if the compressive stress reaches a critical value ($\sim$ 3GPa), the hBN phase is transformed to cBN phase, and the critical stress ($\sim$ 3GPa) is necessary for the formation of cBN phase. Making use of the thermodynamic boundary between graphite and diamond, McKenzie *et al.* determined the critical stress.

Since McKenzie *et al.* proposed the stress model, the BN phase diagram of Bundy-Wentorf has come into debate.[22] Because it is uncertain whether the thermodynamic boundary in the BN system will mimic that of carbon. Furthermore, the cBN film minimum stress of curve d in fig. 3 is 0.5 GPa, which is different from that the compressive stress model predicts. The observed phenomenon that the cBN content falls off below a critical stress, is not predicted by the stress model. In contrast, our calculation can well account for the two experimental results, as discussed above.

IV. CONCLUSIONS

The Gibbs free energy including elastic strain energy of the cBN film in biaxial stress field is calculated. The calculated results indicate that the compressive stress has an effect on the formation of cBN phase in the thin BN films. At a given substrate temperature, there is a compressive stress threshold, below which cBN is the thermodynamically stable phase, and above which hBN is the thermodynamically stable phase. At room temperature the compressive stress threshold is 9.5 GPa. Our calculated results also indicate that cBN can be formed at very low compressive stress, and the cBN phase is thermodynamically stable at the standard conditions. Based on the calculated results, it is concluded that the high compressive stress of the cBN films is the result, not the casuse, of cBN formation. These conclusions are different from that predicted by the compressive stress model; however, they could well account for the experimental results. We think further study is needed to be done by *in situ* stress measurements during the depositon of cBN films.

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