Получение, структура, свойства

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Analysis of direct transformation from graphite to diamond crystal

The lattice parameters of cubic diamond and rhombohedral graphite under the probable direct transformation synthesis conditions have been obtained by means of linear expansion coefficient and elastic constant. Based on the empirical electron theory in solid and molecules, the valence electron structures (VESs) of graphite and diamond, the covalent electron densities (CEDs), and the relative electron density differences (REDDs) of the diamond growth interfaces have been calculated. It has been found that the REEDs of graphite/diamond interfaces were awfully large and the CEDs were discontinuous at the first order approximation. Not any meaningful atomic state of graphite structure, which satisfied the bond length difference formula, existed on the detonation synthetic conditions. Accordingly, it was considered that the direct transformation from graphite to diamond could not come true from the perspective of VES. In addition, the mechanism of synthesis diamond by explosive detonation was discussed based on the VESs of graphite and diamond.

Keywords: *graphite, diamond, direct transformation, HPHT, VES.*

INTRODUCTION

Since the diamond particles were synthesized by G.E. in 1954, the transformation mechanism of graphite to diamond crystals at high pressure and high temperature (HPHT) has been the focus of researchers. But there have been no clear explanation so far. The solid direct transformation theory believed that the graphite structure could be transformed into diamond structure directly without decomposition [1–3]. There are two kinds of graphite: hexagonal and rhombohedral. Gou et al. believed that only rhombohedral graphite could be directly transformed into diamond. Except synthesis at HPHT, graphite can directly transform into diamond by explosive detonation, but the detonation synthesis mechanism remains unclear too. Therefore, the study on whether the carbon source for diamond growth comes from graphite structure direct transformation under the probable direct transformation synthesis conditions will make clear the direct transformation mechanism further.

The empirical electron theory (EET), which is established on the basis of Pauling's valence bond theory and the energy band theory, has been successfully applied to many research areas. Based on the lattice parameters and its crystal structure, the valence electron structures (VESs) of solid or molecular system can be confirmed by means of the bond-length-difference (BLD) method, and the covalent electron density (CED) of a certain crystal plane can also be calculated [4, 5]. The carbon source for diamond crystal growth definitely comes from the transformation of carbon source phase (CSP), and the smaller the value of the relative electron density differences (REDDs) of interfaces between diamond naked planes and corresponding CSP planes, the more similar the VESs of the two adjacent planes, the lower the driving force for C atoms transforming from CSP into diamond growth planes. The calculation of VESs is established on the crystal lattice parameters [6]. Because the direct transformation from graphite to diamond occurred at HPHT, the calculation of VESs at HPHT can not be carried out according to the lattice parameters, which are determined at normal temperature and pressure. However, in this paper, the lattice parameters of graphite and diamond at HPHT were confirmed by the use of a linear expansion coefficient and elastic constant. Then, the VESs of graphite, diamond and the REEDs of graphite/diamond interfaces were calculated, and the possibility of the direct transformation from graphite to diamond in different synthetic conditions, by means of the REEDs analysis of graphite/diamond interfaces, the diamond growth direct transformation mechanism was discussed from the perspective of VES. Besides, the mechanism of diamond synthesis by explosive detonation was discussed based on the VESs of graphite and diamond.

CRYSTAL STRUCTURE OF GRAPHITE AND DIAMOND

The BLD method is the basic method to calculate the VESs in EET. The precondition of calculation is to confirm the unit crystal structure, lattice parameter, and atomic coordinate.

The rhombohedral graphite with an ABCABC stacking order is more likely to be transformed into cubic diamond structure [7]. Its space group is D_{3d}^5-$R\bar{3}m$ and the lattice parameters at room temperature (RT) are $a_0 = 0.24612$ nm and $c_0 = 1.0062$ nm. The most common structure of diamond crystals synthesized at HPHT is cubic. Its space group is O_A^7-Fd3m and lattice parameters at RT are $a_0 = 0.35668$ nm.

The direct transformation from graphite to diamond could not come true at any temperature and any pressure. The conditions of static pressure synthesis without catalyst are $p = 12$–13 GPa and $T = 3000$–4000 K [8]. The conditions of explosive detonation synthesis are $p > 30$ GPa and $T = 2500$–4000 K [9–11]. In this paper, the calculations are carried out on the three conditions (Con1, Con2, Con3) as shown in Table 1.

Table 1. Lattice parameters of graphite and diamond under different synthesis conditions

No.	p, GPa	T, K	Lattice parameters, nm		
			graphite		diamond
			a axis	c axis	
1	12.5	4000	0.24525	0.80017	0.36169
2	13	3000	0.24504	0.74343	0.35856
3	35	3000	0.24244	0.14569	0.35264

Linear expansion coefficient (LEC) is a material's inherent attribute, which shows the impact of temperature on material's length (or volume). According to the LEC, the relationship between lattice parameter and temperature can be defined [12, 13]. Based on the experimental results achieved by Morgan and Reeber [14–17], the relationships between linear expansion coefficient and temperature of graphite and diamond were given separately in this paper. For the space limitation, the detailed calculation process is not listed.

Hooke's law considers that the stress is proportional to strain in a solid when the stress is less than proportional limit. The generalized Hooke's law can be achieved under the condition of three-dimensional stress and strain state. The lattice parameter and pressure can be contacted with each other by the coefficients in generalized Hooke's law (elastic constant) [18].

By fitting the effects of temperature and pressure on lattice parameter, the lattice parameter of a crystal at HPHT can be obtained. Table 1 shows the lattice parameters of graphite and diamond under three synthesis conditions.

VESS AND CEDS OF GRAPHITE, DIAMOND AND REDDS OF INTERFACES

VESs of graphite and diamond

The VESs of rhombohedral graphite and diamond under the three conditions shown in Table 1 are calculated by the BLD method based on EET [7]. The results are listed in Tables 2–6, respectively.

Table 2. VES of graphite on the condition of Con1

Bond	l	$D_{n\alpha}$, nm	$\overline{D}_{n\alpha}$, nm	n_α	D_n, nm
D_A^{C-C}	3	0.14160	0.14612	1.23382	0.00452
D_B^{C-C}	6	0.24525	0.24977	0.04280	0.00452
D_C^{C-C}	3	0.28319	0.28771	0.01250	0.00452
D_D^{C-C}	1	0.37463	0.37915	0.00064	0.00452
D_E^{C-C}	9	0.40009	0.40461	0.00028	0.00452
D_F^{C-C}	6	0.42440	0.42892	0.00013	0.00452
D_G^{C-C}	6	0.46927	0.47379	0.00003	0.00452
D_H^{C-C}	9	0.49017	0.49469	0.00002	0.00452
C: $\sigma = 6$, $R_6(1) = 0.0763$ nm, $n_c^6 = 4.0000$, $n_c = 4.0000$, $\beta = 0.0710$ nm, $\sigma_N = 1$					

Table 3. VES of graphite on the condition of Con2

Bond	l	$D_{n\alpha}$, nm	$\overline{D}_{n\alpha}$, nm	n_α	D_n, nm
D_A^{C-C}	3	0.14147	0.14617	1.23196	0.00470
D_B^{C-C}	6	0.24504	0.24974	0.04284	0.00470
D_C^{C-C}	3	0.28295	0.28765	0.01253	0.00470
D_D^{C-C}	1	0.37430	0.37900	0.00065	0.00470
D_E^{C-C}	9	0.37172	0.37642	0.00070	0.00470
D_F^{C-C}	6	0.39773	0.40243	0.00030	0.00470
D_G^{C-C}	6	0.44522	0.44992	0.00007	0.00470
D_H^{C-C}	9	0.46715	0.47185	0.00003	0.00470
C: $\sigma = 6$, $R_6(1) = 0.0763$ nm, $n_c^6 = 4.0000$, $n_c = 4.0000$, $\beta = 0.0710$ nm, $\sigma_N = 1$					

Table 4. VES of graphite on the condition of Con3

Bond	l	$D_{n\alpha}$, nm	$\overline{D}_{n\alpha}$, nm	n_α	D_n, nm
D_A^{C-C}	3	0.13997	0.24727	0.04641	0.10730
D_B^{C-C}	6	0.24244	0.34974	0.00167	0.10730
D_C^{C-C}	3	0.27995	0.38725	0.00050	0.10730
D_D^{C-C}	1	0.15779	0.26509	0.02604	0.10730
D_E^{C-C}	9	0.37033	0.47763	0.00003	0.10730
D_F^{C-C}	6	0.07285	0.18015	0.40918	0.10730
D_G^{C-C}	6	0.25315	0.36045	0.00118	0.10730
D_H^{C-C}	9	0.28927	0.39657	0.00037	0.10730
C: $\sigma = 6$, $R_6(1) = 0.0763$ nm, $n_c^6 = 4.0000$, $n_c = 4.0000$, $\beta = 0.0710$ nm, $\sigma_N = 0$					

According to the calculation results ($\Delta D = 0.1073$ nm $>> 0.005$ nm) as shown in Table 4, it can be found that there isn't any meaningful atomic state of graphite structure on the condition of explosive detonation (Con 3), so the VES of diamond under the condition can't be defined.

Table 5. VES of diamond on the condition of Con1

Bond	l	$D_{n\alpha}$, nm	$\overline{D}_{n\alpha}$, nm	n_α	D_n, nm
D_A^{C-C}	4	0.15662	0.15698	0.86750	0.00036
D_B^{C-C}	12	0.25575	0.25611	0.03484	0.00036
D_C^{C-C}	12	0.29990	0.30026	0.00832	0.00036
D_D^{C-C}	6	0.36169	0.36205	0.00112	0.00036
D_E^{C-C}	12	0.39414	0.39450	0.00039	0.00036
D_F^{C-C}	8	0.44298	0.44334	0.00008	0.00036
C: $\sigma = 6$, $R_6(1) = 0.0763$ nm, $n_c^6 = 4.0000$, $n_c = 4.0000$, $\beta = 0.0710$ nm, $\sigma_N = 2$					

Table 6. VES of diamond on the condition of Con2

Bond	l	$D_{n\alpha}$, nm	$\overline{D}_{n\alpha}$, nm	n_α	D_n, nm
D_A^{C-C}	4	0.15526	0.15711	0.86392	0.00185
D_B^{C-C}	12	0.25354	0.25539	0.03567	0.00185
D_C^{C-C}	12	0.29730	0.29915	0.00863	0.00185
D_D^{C-C}	6	0.35856	0.36041	0.00118	0.00185
D_E^{C-C}	12	0.39073	0.39258	0.00042	0.00185
D_F^{C-C}	8	0.43914	0.44099	0.00009	0.00185
C: $\sigma = 6$, $R_6(1) = 0.0763$ nm, $n_c^6 = 4.0000$, $n_c = 4.0000$, $\beta = 0.0710$ nm, $\sigma_N = 2$					

CEDs of graphite, diamond, and REDDs of interfaces:

If all covalent electrons in a structure unit are distributed on its all covalent bonds [5], the number of covalent electrons on one crystal plane should be equal to that of all covalent bonds on this plane [7]. According to the theory, the CED of a certain crystal plane can be calculated.

The REDD of an interface can be defined as:

$$\Delta\rho(\%) = \frac{|\rho_1 - \rho_2|}{(\rho_1 + \rho_2)/2} \times 100\,\%.$$

Then the CEDs of common carbon crystal planes in rhombohedral graphite and diamond structure and REDDs of rhombohedral graphite/diamond interfaces on the condition of Con1 and Con2 are calculated and the results are shown in Tables 7–10, respectively.

Table 7. CED of common planes in graphite on the condition of Con1 and Con2

Crystal plane	$\sum n_c$		S, nm^2		ρ, nm^{-2}	
	Con1	Con2	Con1	Con2	Con1	Con2
G(001)	7.9992	7.98882	0.05209	0.05200	153.56498	153.63115
G(100)	0.17188	0.17304	0.19624	0.18217	0.87587	0.94988
G(110)	7.4823	7.47708	0.33990	0.31553	22.01324	23.69689
G(113)	1.2467	1.24537	0.06235	0.05866	19.99519	21.23031

Table 8. CED of common planes in diamond on the condition of Con1 and Con2

Crystal plane	$\sum n_c$		S, nm^2		ρ, nm^{-2}	
	Con1	Con2	Con1	Con2	Con1	Con2
D(100)	0.288	0.294	0.130	0.129	2.1991	2.2929
D(111)	0.418	0.428	0.113	0.111	3.6903	3.8444
D(110)	7.297	7.278	0.185	0.182	39.4430	40.0316

Table 9. REDDs of graphite/diamond interface on the condition of Con1 (%)

	G(001)	G(100)	G(110)	G(113)
D(100)	194.4	86.1	163.7	160.4
D(111)	190.6	123.3	142.6	137.7
D(110)	118.3	191.3	56.7	65.4

Table 10. REDDs of graphite/diamond interface on the condition of Con2 (%)

	G(001)	G(100)	G(110)	G(113)
D(100)	194.1	82.8	164.7	161
D(111)	190.2	120.7	144.2	138.7
D(110)	117.3	190.7	51.3	61.4

D means diamond, G means graphite.

DISCUSSION

Liu et al. suggested that the CED between the heterogeneous interfaces should be continuous. If the REDD value of an interface is less than 10 %, it is approved that the CED between the heterogeneous interfaces is continuous at the first order approximation. The smaller the REDDs value of interfaces, the more similar the VESs of the two adjacent planes, the lower the driving force for one structure transforming into another [7]. The carbon source for diamond crystal growth definitely comes from the transformation of CSP, the continuity of CED between diamond naked planes and corresponding graphite planes is just the essential condition for diamond growth.

In crystallography, the naked crystal planes just are the planes whose growth rate is faster in the course of crystal growth. In diamond, (100), (110) and (111) planes are the main crystal growth planes. As shown in Table 9 and Table 10, the REDDs of all graphite/diamond interfaces calculated in this paper are far more than 10 %, that is to say, the VESs difference of the adjacent planes between graphite and diamond are so large that the driving force for graphite direct transforming into diamond will be great. Through the detail researches on metallic film surrounding as-grown diamond by Transmission Electron Microscope (TEM), Raman, and other experimental methods, Xu discovered that there was not diamond structure in the entire metallic film, and also not graphite structure in the inner of the metallic film, which was quite similar to diamond. The rich-carbon-content phase in the metal film/diamond interface was Me_3C [19–23]. Li considers that the carbon sources forming diamond may come from the decomposition of Me_3C type carbides, because three among those of Fe_3C/diamond interfaces are less than 10 % in their calculation from the view point of VES [24] (lattice parameters used in the calculation are determined at normal temperature and pressure). Then from the perspective of VES, the direct transformation from graphite to diamond could not come true. During the course of graphite transforming into diamond, the synthesis success needs some transition mesophases or the participation of catalyst. The transition mesophase (carbides) may be generated at first before carbon atoms, which come from graphite structures' decomposition, nucleate to the nucleus of diamond crystal, and the nucleating carbon sources of diamond crystal may come from the decomposition of carbides.

As to the diamond synthesis mechanism by explosive detonation, some researchers suggested that this transformation process as follows may be undergone: the explosive molecules were decomposed into various atoms (C, H, O, N) in detonation zone firstly; and then, the diamond atomic groups were made up by the excessively aggregated carbon atoms combining with each other; finally, the atomic groups transformed into stable diamond structure [25]. Other researchers insisted that because of the supersaturation of the free carbon atoms in detonation zone, carbon droplets generated and then the carbon droplets crystallized in diamond crystal [26]. In the two synthesis mechanism explanations above, the disappearance of graphite structure is acknowledged and diamond structures are originated from the reconstruction of carbon atoms. According to the calculation as shown in Table 4, any meaningful atomic state of graphite structure which satisfied BLD formula does not exist on the detonation synthetic conditions. So from the perspective of VES graphite structure can't exist on the detonation synthetic conditions, which is in accordance with the synthesis mechanism above.

CONCLUSIONS

According to the calculation and analysis from the perspective of VES, it is shown that the REDDs of the graphite/diamond interfaces are far more than 10 %,

the diamond structure could not come from graphite structure's direct transformation. During the course of graphite transforming into diamond, the synthesis success needs some transition mesophases or the participation of catalyst. Any meaningful atomic state of graphite structure, which satisfies BLD formula, does not exist on the detonation synthetic conditions. From the perspective of VES, it is proved that diamond crystals are originated from the reconstruction of carbon atoms on the detonation synthetic conditions.

Визначено параметри решіток алмазу кубічного габітусу і ромбоедричної графіту в умовах ймовірного прямого перетворення з використанням коефіцієнта лінійного розширення і пружною постійною. На основі емпіричної теорії електронів в твердому тілі і молекулах було розраховано структуру валентних електронів графіту і алмазу, щільність ковалентних електронів і відносні відмінності в щільності електронів в міжфазних межах зростання алмазу. Виявлено, що відносна різниця в щільності електронів в міжфазній межі графіт/алмаз дуже велика, а щільність ковалентних електронів переривчаста при апроксимації першого порядку. В умовах детонаційного синтезу не існує жодного значимого атомного стану структури графіту, яке б відповідало різниці у формулі довжини зв'язку. Відповідно, вважали, що пряме перетворення графіту в алмаз не може статися через структуру валентних електронів. Крім того, на основі структури валентних електронів графіту і алмазу обговорено механізм синтезу алмазу вибуховою детонацією.

Ключові слова: графіт, алмаз, пряме перетворення, високий тиск– висока температура, структура валентних електронів.

Определены параметры решеток алмаза кубического габитуса и ромбоэдрического графита в условиях вероятного прямого превращения с использованием коэффициента линейного расширения и упругой постоянной. На основе эмпирической теории электронов в твердом теле и молекулах были рассчитаны структура валентных электронов графита и алмаза, плотность ковалентных электронов и относительные различия в плотности электронов в межфазных границах роста алмаза. Обнаружено, что относительная разница в плотности электронов в межфазной границе графит/алмаз очень большая, а плотность ковалентных электронов прерывистая при аппроксимации первого порядка. В условиях детонационного синтеза не существует ни одного значимого атомного состояния структуры графита, которое бы соответствовало разнице в формуле длины связи. Соответственно, полагали, что прямое превращение графита в алмаз не может произойти из-за структуры валентных электронов. Кроме того, на основе структуры валентных электронов графита и алмаза обсужден механизм синтеза алмаза взрывной детонацией.

Ключевые слова: графит, алмаз, прямое превращение, высокое давление–высокая температура, структура валентных электронов.

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