

# Valence Electron Structure Analysis of Graphite-Diamond Transformation at HPHT

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## Abstract

The valence electron structures of diamond, graphite and their common crystal planes at super high temperature and pressure (3000 K and 10 GPa) were calculated by the experimental electron theory of solid and molecule (EET). The electron density continuity of interfaces between diamond and graphite was analysed. It was found that the electron densities were continuous, which satisfies the boundary conditions of diamond crystal growth. The calculation method and theory involved in this paper provides the research of diamond crystal growth a new perspective.

## Keywords

Diamond, Graphite, Valence Electron Structure, Electron Density, Interface

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## 1. Introduction

Synthesizing diamond is essentially creating some conditions to transform graphite atom structure ( $sp^2$  hybridization) into diamond atom structure ( $sp^3$  hybridization). Although the technology of synthesizing diamond at high pressure and high temperature (HPHT) has been developed for half a century since the first diamond was synthesized, the transformation mechanism hasn't been clarified. The key problem of crystal growth is about growth interface. The boundary condition of atoms in material is keeping the electron density of interface continuous to meet the requirement of quantum mechanics as mentioned by Cheng [1]. Accordingly, the electron density between planes in carbon source phase and planes in diamond crystal should be continuous, which is the boundary condition of diamond growth.

Based on known crystal structure, the valence electron structure (VES) of solids and molecules can be calculated according to the empirical electron theory (EET), and the covalent electron density of a certain crystal plane can also be calculated [2]. The method was proposed in Ref. [3].

Compared to other electron theories, the calculation method of EET is more simple and easy to realize programmed, and has been widely used in many studies, [4-7], such as crystal growth, phase transformation, film oriented growth and so on. The authors [8-10] have used EET to analyse the VESs of diamond and graphite and their electron density continuity at normal temperature and pressure and at high pressure and temperature with catalysts, and also analyse the electron density community between  $Fe_3C$  type carbides (existed during diamond synthesis with metallic catalyst) and diamond. The results show that the electron densities of interfaces between diamond and graphite are not continuous, which cannot satisfy the boundary condition of diamond growth. However the electron densities of interfaces between diamond and carbides are continuous, which satisfies the boundary condition of diamond growth. In this paper we will use EET to analyse the transformation between graphite and diamond at super high pressure and temperature (3000 K and 10 GPa) without catalysts, and further verify the feasibility of using EET to analyse the diamond crystal growth.

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## 2. Calculation of the VESs of Diamond and Graphite

### 2.1. The VES of Diamond

The diamond crystals synthesized at HPHT are almost cubic diamond whose crystal structure is showed in fig. 1. Besides 4 atoms in face-centred cubic structure, there are 4 atoms whose atom positions are  $(1/4, 1/4, 1/4)$ ,  $(1/4, 3/4, 3/4)$ ,  $(3/4, 3/4, 1/4)$  and  $(3/4, 1/4, 3/4)$  in the interior. The temperature and pressure needed to synthesize diamond directly without catalysts are 3000 K and 10 GPa. Commonly, the lattice constants of crystal provided in references are obtained at normal temperature and pressure. However, the crystal structure expands or shrinks with the promotion of temperature and pressure, which will bring on the change of lattice constants. The lattice constant of diamond at 3000 K and 10 GPa is  $a=0.35886$  nm which is calculated with linear thermal expansion coefficient and elastic modulus by the method mentioned by author in Ref. [8].

The VES of diamond can be calculated by the bond length difference method of EET which has been introduced and used by author in Ref. [8-10], and the results are shown in table 1.

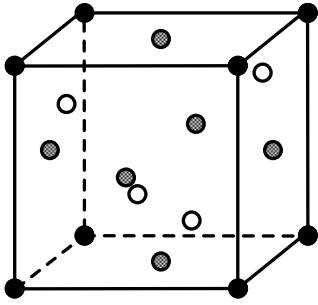


Figure 1. Crystal structure of cubic diamond.

Table 1. Valence electron structure of cubic diamond.

Bond	$I_\alpha$	$D_{n\alpha}/nm$	$\bar{D}_{n\alpha}/nm$	$n_\alpha$	$D_n/nm$
A	4	0.15539	0.15980	0.76166	0.00441
B	12	0.25375	0.25816	0.03260	0.00441
C	12	0.29755	0.30196	0.00787	0.00441
D	6	0.35886	0.36327	0.00108	0.00441
E	12	0.39106	0.39547	0.00038	0.00441
F	8	0.43951	0.44392	0.00008	0.00441

C:  $\sigma=6$ ,  $R_\sigma(1)=0.0763$  nm,  $n_c^6=4.0000$ ;  $\beta=0.0710$ ,  $\sigma_N=3$

$\sigma$ , Hybrid level;  $R_\sigma(1)$ , bond radius in  $\sigma$  hybrid level;  $n_{ca}$ , total covalent electron number in  $\sigma$  hybrid level;  $I_\alpha$ , equivalent bond number;  $D_{m\alpha}$ , experimental bond length;  $D_{n\alpha}$ , theoretical bond length;  $n_\alpha$ , covalent electron pairs;  $\Delta D_{n\alpha}$ , bond length difference;  $\beta$ , coefficient;  $\sigma_N$ , groups of the state in which atoms exist.

### 2.2. The VES of Graphite

The bonding characteristics of  $sp^2$  hybrid orbital determine

the planar hexagonal layered structure of graphite. The stacking of these layer planes occurs in two slightly different ways resulting in two kinds of graphite: the hexagonal (AB type) and rhombohedral (ABC type) graphites, as shown in fig. 2. The most common stacking sequence of the graphite crystal is hexagonal with an ABAB stacking order, in which the carbon atoms in every other layer are superimposed over each other. However, some research [11] consider that during the diamond synthesizing at HPHT hexagonal graphite is transformed into rhombohedral graphite firstly and then into cubic diamond. In this paper the two types of graphite structure are both analysed.

At 3000 K and 10 GPa, the lattice constants of AB type graphite are  $a=0.24551$  nm and  $c=0.54981$  nm, and those of ABC type graphite are  $a=0.24551$  nm and  $c=0.82471$  nm, which are calculated with linear thermal expansion coefficient [12] and elastic modulus by the method mentioned by author in Ref. [8]. Their VESs are calculated by the bond length difference method of EET, and the results are shown in tables 2 and 3, respectively.

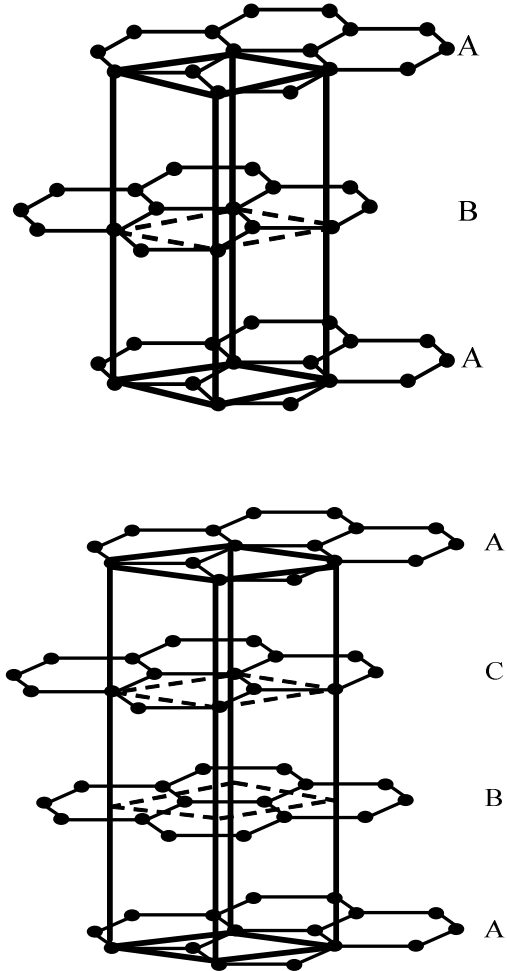


Figure 2. Crystal structure of AB type and ABC type graphite.

**Table 2.** The VES of AB type graphite.

Bond	$I_\alpha$	$D_{n\alpha}/\text{nm}$	$\bar{D}_{n\alpha}/\text{nm}$	$n_\alpha$	$D_n/\text{nm}$
A	3	0.14175	0.14669	1.22107	0.00494
B	6	0.24551	0.25045	0.04816	0.00494
C	3	0.28349	0.28843	0.01221	0.00494
D	6	0.37502	0.37996	0.00063	0.00494
E	2	0.27490	0.27984	0.01614	0.00494
F	6	0.30930	0.31424	0.00529	0.00494
G	12	0.36858	0.37352	0.00077	0.00494
H	6	0.39489	0.39983	0.00033	0.00494

C:  $\sigma=6$ ,  $R_\alpha(1)=0.0763$  nm,  $n_c^6=4.0000$ ;  $\beta=0.0710$ ,  $\sigma_N=1$

**Table 3.** The VES of ABC type graphite.

Bond	$I_\alpha$	$D_{n\alpha}/\text{nm}$	$\bar{D}_{n\alpha}/\text{nm}$	$n_\alpha$	$D_n/\text{nm}$
A	3	0.14175	0.145655	1.21668	0.00480
B	6	0.24551	0.25031	0.04205	0.00480
C	3	0.28349	0.28829	0.01227	0.00480
D	6	0.37502	0.37982	0.00063	0.00480
E	1	0.27490	0.27970	0.01621	0.00480
F	6	0.30930	0.31210	0.00531	0.00480
G	9	0.36858	0.37338	0.00078	0.00480
H	6	0.39489	0.39969	0.00033	0.00480

C:  $\sigma=6$ ,  $R_\alpha(1)=0.0763$  nm,  $n_c^6=4.0000$ ;  $\beta=0.0710$ ,  $\sigma_N=1$

### 3. Calculation of the VESs of Diamond/Graphite Interfaces

#### 3.1. The VESs of Crystal Planes in Graphite and Diamond Structures

EET suggests that all covalent electrons in a structure unit should be distributed on its all covalent bonds, and the number of covalent electrons on one crystal plane should be equal to all covalent electrons of covalent bonds on this plane. So the covalent electron density of a certain crystal plane can be calculated as follows:

$$\rho = \frac{\sum n_c}{S} = \frac{\sum I_\alpha n_\alpha}{S} \quad (1)$$

In eqn. (1)  $\sum n_c$  is the valence electron number of the crystal plane;  $n_\alpha$  and  $I_\alpha$  represent the valence electron number and equivalent bond number of bond  $\alpha$  on the plane;  $S$  means the plane area;  $\rho$  represents the electron density of crystal plane.

The bonds and the equivalents bond numbers of (100), (110), and (111) planes in diamond structure are shown in table 4, and the valence electron numbers of the bonds are given in table 1. Accordingly, the electron density of these planes can be calculated by eqn. (1) and the results are shown in table 4. By the same method, the electron densities of common planes in the two kinds of graphite are calculated and the results are shown in tables 5 and 6.

**Table 4.** The VESs of common planes in cubic diamond structure.

Crystal plane	Bond	$I_\alpha$	$\rho/\text{nm}^{-2}$
D(100)	B	8	2.09225
	D	8	
D(111)	B	12	3.50757
	A	8	
D(110)	B	8	35.31298
	C	8	
	D	8	
	E	8	
	F	16	

**Table 5.** The VESs of crystal planes in AB type graphite.

Crystal plane	Bond	$I_\alpha$	$\rho/\text{nm}^{-2}$
G(0001)	A	6	151.67816
	B	12	
	C	6	
G(10 $\bar{1}$ 0)	B	4	1.95110
	E	4	
	G	8	
G(11 $\bar{2}$ 0)	A	6	32.24124
	C	6	
	E	6	
	F	18	
	H	18	
G(10 $\bar{1}$ 2)	B	2	1.08144
	G	2	
	A	1	
G(11 $\bar{2}$ 2)	C	1	19.32115
	F	2	
	G	4	

**Table 6.** The VESs of crystal planes in ABC type graphite.

Crystal plane	Bond	$I_\alpha$	$\rho/\text{nm}^{-2}$
G(0001)	A	6	150.74713
	B	12	
	C	6	
G(10 $\bar{1}$ 0)	B	4	1.50941
	E	2	
	G	4	
G(11 $\bar{2}$ 0)	A	6	32.39001
	C	6	
	E	6	
	F	18	
	H	18	
G(10 $\bar{1}$ 2)	B	2	0.94662
	G	2	
	A	1	
G(11 $\bar{2}$ 3)	C	1	19.57685
	F	4	
	G	4	

#### 3.2. The Relative Electron Density Difference of Graphite/Diamond Interfaces

Thomas-Fermi-Dirac theory by Cheng [1] considers the electron density being continuous as the boundary criterion of atoms, so the electron density should also be continuous

on the contacting surfaces, which has been proved by Cheng from the first principle. The calculation of EET is at the first order of approximation. So if the difference of covalent electron density ( $\Delta\rho$ ) of two adjacent planes is less than 10%, it is assumed that the electron density of interface is continuous at the first order of approximation. The lower the  $\Delta\rho$  of two adjacent planes, the closer the covalent electron structure of interface, and the lower the driving force for transforming one structure into another. This density continuity is just the boundary condition for diamond growth. The relative electron density difference (REDD) between two adjacent planes can be calculated as following.

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

Tables 7 and 8 show the REDD ( $\Delta\rho$ ) between common planes in diamond and planes in the two kinds of graphite.

## 4. Discussion

Many experimental and calculational results show that the larger the difference of electron density on interface, the greater the interface stress. The reason is that the larger difference of electron density on interface result in the dramatic changes in electronic state of atoms on both sides of the interface, and the atom radius also deviate greatly from the radius of atom in stable state.

The transformation of graphite into diamond not only needs add external pressure to change C atoms' radius and improve their boundary electron density, at the same time needs across a high chemical potential barrier to change the electronic structure of C atoms. At normal temperature and pressure and high temperature and pressure with catalyst (about 1600 K and 5.5 GPa), the electron density between graphite and diamond are discontinuous as shown in the author's study [7]. So it's difficult to form continuous growth interface, and valence electrons need very large driver force to transfer from graphite to diamond. It means the direct transformation from graphite structure into diamond structure needs great energy, and the pressure and temperature of the catalyst method can't supply this energy. However, it can be seen from tables 7 and 8 that at 3000 K and 10 GPa, the REDDs between several planes of graphite and planes in diamond, such as G(10 $\bar{1}$ 0)/D(100) and G(11 $\bar{2}$ 0)/D(110) interfaces in table 7, and G(11 $\bar{2}$ 0)/D(110) interface in table 8, are less than 10% as shown with bold text in the tables. That is, the electron density of the interface between the graphite and diamond is continuous at the first approximation. It satisfies the boundary condition of diamond growth and means that

the graphite structure can transform into the diamond structure directly, which agrees with the diamond synthesis experiments.

**Table 7.** The REDD between planes in diamond and AB type graphite (%).

	<b>D(100)</b>	<b>D(111)</b>	<b>D(110)</b>
G(0001)	183.1	172.5	23.8
G(10 $\bar{1}$ 0)	<b>6.98</b>	85.2	185.4
G(11 $\bar{2}$ 0)	174.2	158.5	<b>8.85</b>
G(10 $\bar{1}$ 2)	81.1	119.4	190.7
G(11 $\bar{2}$ 2)	158.7	135.4	69.0

**Table 8.** The REDD between planes in diamond and ABC type graphite (%).

	<b>D(100)</b>	<b>D(111)</b>	<b>D(110)</b>
G(0001)	188.6	181.2	62.2
G(10 $\bar{1}$ 0)	75.2	114.9	190.1
G(11 $\bar{2}$ 0)	159.1	135.8	<b>8.63</b>
G(10 $\bar{1}$ 2)	143.0	164.0	116.9
G(11 $\bar{2}$ 3)	153.5	127.7	80.6

## 5. Conclusions

The calculation and analysis of the VESs diamond and graphite and the electron density continuity of interfaces show that the electron density of the interfaces between the graphite and diamond are continuous at the super high temperature and pressure of 3000 K and 10 GPa, which satisfies the boundary condition of diamond growth. It means that the graphite structure can transform into the diamond structure directly at this temperature and pressure.

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