Diamond & Related Materials 19 (2010) 1341–1347

Contents lists available at ScienceDirect

Diamond & Related Materials

journal homepage: www.elsevier.com/locate/diamond

Atomic structure and mechanical properties of BC_2N superlattice

Bi-Ru Wu [a], Zhi-Quan Huang [b], Wan-Sheng Su [c], Yun-Yi Hsieh [b], Feng-Chuan Chuang [b],*

[a] *Center for General Education, Chang Gung University, Kueishan 333, Taiwan*
[b] *Department of Physics, National Sun Yat-sen University, Kaohsiung 804, Taiwan*
[c] *Center for General Education, Tainan University of Technology, Tainan 710, Taiwan*

ARTICLE INFO

Article history:
Received 3 November 2009
Received in revised form 8 April 2010
Accepted 22 June 2010
Available online 30 June 2010

Keywords:
density functional theory
superhard materials
carbon-based materials
mechanical property
greedy algorithm

ABSTRACT

Structural motifs for the BC_2N superlattices were identified from a systematic search based on a greedy algorithm. Using a tree data structure, we have retrieved seven structural models for c-BC_2N $1\times1\times1$ lattice which were identified previously by Sun et al. [Phys. Rev. B 64, 094108 (2001)]. Furthermore, the atomic structures with the maximum number of C–C bonds for c-BC_2N $2\times2\times2$, $3\times3\times3$, and $4\times4\times4$ superlattices were found by imposing the greedy algorithm in the tree data structure. This new structural motif has not been previously proposed in the literature. A total of up to 512 atoms in the c-BC_2N superlattice are taken into consideration. The atoms in these superlattices are in diamond-like structural form. Furthermore, the C atoms, as well as B and N atoms, form the octahedral motif separately. The octahedral structure consisting of C is bounded with {111} facets, and each facet is interfaced to a neighboring octahedral structure consisting of B and N atoms. The electronic and mechanical properties of newly identified low energy structures were analyzed.

1. Introduction

Superhard materials have gained much attention from industries due to their high compressive strength and thermal conductivity. Diamond, as the hardest material in existence, is widely used as abrasives. However, the thermal and chemical instabilities of diamond have limited its application as an abrasive on ferrous alloys. Looking for new superhard materials is an intriguing challenge. Recently, BC_2N, a simple alloy of diamond and c-BN, has been singled-out as the likeliest superhard substance that has the ability to resist the thermal and chemical instabilities. Not only does the synthesized BC_2N crystal possess the better thermal and chemical stabilities than diamond but it also has a higher hardness than cubic boron nitride (c-BN) [1,2].

Recently, certain successful syntheses of ternary c-BC_2N compound via high-pressure and high-temperature methods have been reported [1,3–12]. Due to different growth conditions and different measurement techniques, there exist diverse findings in experiments. However, the results can still be classified into two groups: the low-density and high-density phases. One can easily see that the lattice constant (3.64 Å) of the low-density c-BC_2N phase is larger than that (3.60 Å) of the high-density phase. In experiments the bulk moduli (340–355 GPa) of the former is smaller than that (276–282 GPa) of the latter [1,3,7]. Nevertheless, the bulk moduli of both phases are smaller than that (368 GPa) of c-BN [1], which is against the initial motivation of designing new superhard materials. Moreover, the study by Dong et al. [9] reported the diverse results for the measurement of bulk modulus ranging from 270 to 420 GPa under the same growth conditions with different techniques. Judging the hardness of a substance based on its experimental bulk moduli might not be sufficient. Another analysis based on the Vickers hardness reveals a different but desirable trend that c-BC_2N is harder than c-BN. The Vickers hardness of c-BC_2N (62–76 GPa) are found to be close to that of diamond (75–100 GPa) and higher than that of c-BN (45–50 GPa) [3,7,9]. The effect of causing the difference in the hardness of c-BC_2N is still unclear. Recently, numerous theoretical studies have proposed atomic structural models of BC_2N: namely, 8-atom cubic diamond based unit cell [2,13], a short period $(C_2)_n(BN)_n$ (111) superlattice [14], and body centered BC_2N [15]. The bulk moduli of these proposed c-BC_2N models are found to be between those of c-BN and diamond. Among these models, the short period $(C_2)_n(BN)_n$ (111) superlattice by Chen et al. [14] is not only energetically more stable but also harder than the c-BC_2N-I in 8-atom cubic lattice identified by Sun et al. [2]. Very recently, an atomic structure search based on the genetic algorithm was performed and $(C_2)_n(BN)_n$ (111) superlattice was found to be one of the best candidates in their search [16,18]. A related study by Fan et al. adopted the divide-and-conquer method [19].

Although many experimental and theoretical efforts had been devoted, the atomic structure of c-BC_2N crystal is still far from being fully comprehended. The difficulty in understanding the atomic structure is that the X-ray diffraction pattern is hardly able to distinguish the element of each atomic position. Therefore, a systematic and efficient algorithm to determine the atomic structures is highly desirable. Recently, predicting the atomic structures of crystals becomes a huge challenge in the materials' design. The predicting methods based

---

* Corresponding author.
E-mail address: fchuang@mail.nsysu.edu.tw (F.-C. Chuang).

0925-9635/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.diamond.2010.06.022

on a genetic algorithm has been developed and utilized extensively in numerous systems [16–18,20–26]. However, for a system with hundreds of atoms, the genetic algorithm usually needs relative larger numbers of populations and generations to evolve in order to obtain the low energy structure [27–29].

In this work, a systematic search based on a greedy algorithm in lieu of the aforementioned genetic algorithm was performed to look for the optimized atomic structures of BC_2N superlattice. A total of up to 512 atoms in the c-BC_2N superlattice is taken into consideration. The atoms included in these superlattices are assumed to be in diamond-like structural form. Our search identified a new structure that has not been proposed previously. Our search found that the C atoms, as well as B and N atoms, form the octahedral motif separately. The octahedral structure consisting of C atoms is bounded with {111} facets, and each facet is interfaced to a neighboring octahedral structure consisting of B and N atoms. The electronic and mechanical properties of newly identified structures were analyzed in detail. The rest of the paper is organized as follows: the greedy algorithm and computational methods are introduced in Section 2. The structural models from our search and the analysis are presented in Section 3. Finally, we summarize our major findings with a brief conclusion in Section 4.

2. Computational methods

2.1. Tree structure and greedy algorithm

The tree structure [30] shown in Fig. 1 is employed as the data structure in order to generate and store all the possible structures. First, we group the elements from 1 to 3, in that carbon, boron and nitrogen atoms are assigned as groups 1, 2, and 3, respectively. We then index the atomic position, p, from 1 to N, where N is the number of atom positions in the superlattice. For a 4×4×4 superlattice, the number of atomic position, N, is 512. In addition, a sequence of placing atoms is defined. As a result, each level in the tree structure shown in Fig. 1 represents the i-th atom being placed in the superlattice. Note that the root of the tree is such that no atom is placed in the structure. For the first level, the first atom is allowed to place at total of N possible positions. Subsequently, each node at L–th level has (N–L) branches. Since a total number of L positions have been previously occupied, this will leave the remaining (N–L) unoccupied sites for the next sequential atom to place. Based on the preceding procedures, we are able to generate all the possible configurations. Note that some of configurations in the data structure are identical. Therefore, by further taking the rotational and translational symmetry into account, the number of distinct configurations in fact will be significantly less. For instance, the first level in the tree structure becomes the only branch left for further tree expansion. Notice that element decorations at the sites are also considered in the structural comparison. The algorithm of structural comparison will be elaborated in the next subsection. We have implemented the preceding algorithm to search the atomic structure for BC_2N 1×1×1 superlattice, and only seven distinct structures are found. Our results are the same as those in Ref. [2].

Such algorithms are also devoted to the cases of 2×2×2, 3×3×3, and 4×4×4. However, due to the growth of the number of candidates, it is in fact a NP problem. A more sophisticated or aggressive algorithm in the tree structure should be utilized to tackle this problem. Here, the algorithm used is called the greedy algorithm which is well-known in the computer algorithm community. Basically, the greedy algorithm [30] makes any choice that seems the best at any moment and then solves the subproblems that arise later. Since the C–C bonds are regarded as the good bonds in a previous study [14], we identify the branch which has the maximum number of C–C bonds and regard it as the best choice at the moment. Note that it is possible that the number of branches at a level with the same maximum number of C–C bonds is more than one. Only the branches of the tree structure with the maximum number of C–C bonds are retained and expanded further. Additional calculations are shown in Fig. 2 to further illustrate that C–C bonds are good bonds.

In the end of placing group 1 element (carbons), only one structure with the maximum number of C–C bonds involved is obtained. Then, the corresponding positions of the elements B and N could be determined. Since the B–N bonds are good bonds and B–B as well as N–N bonds are bad ones, the best choice is to place the B and N atoms, respectively, at the (0, 0, 0) and (1/4, 1/4, 1/4) sites of the rest of the unoccupied atomic positions and vice versa. Both types of structures were examined further using first-principles calculations.

2.2. Choice of fitness function

It is impractical to perform the first-principles calculations on all the structural motifs. A quick and efficient method of ruling out the unstable structures is to use an empirical classical potential to evaluate their total energies. A similar idea was used in the genetic algorithm to look up the atomic structures of atomic clusters and surfaces [27,28,38–42]. In this work, we adopt an alternative based on counting the numbers of specific chemical bonds instead. Since the structure of the lower energy BC_2N

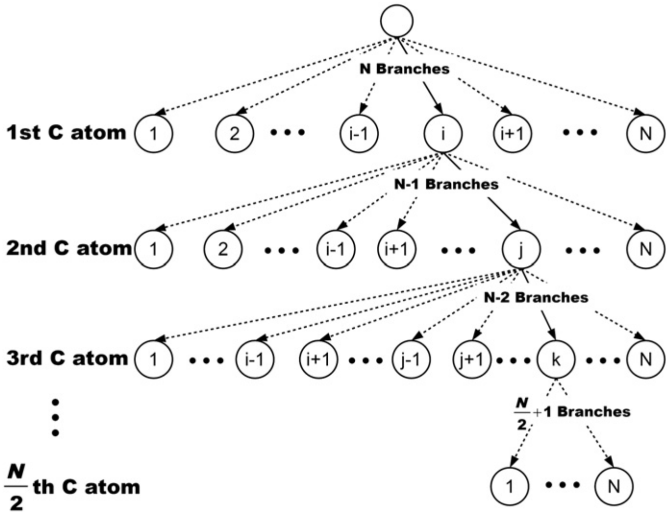

Fig. 1. The illustration of the tree structure used in this study. The solid arrows indicate the branches with the maximal number of the C–C bonds below certain nodes, whereas the dashed arrows indicate the rest of the branches.

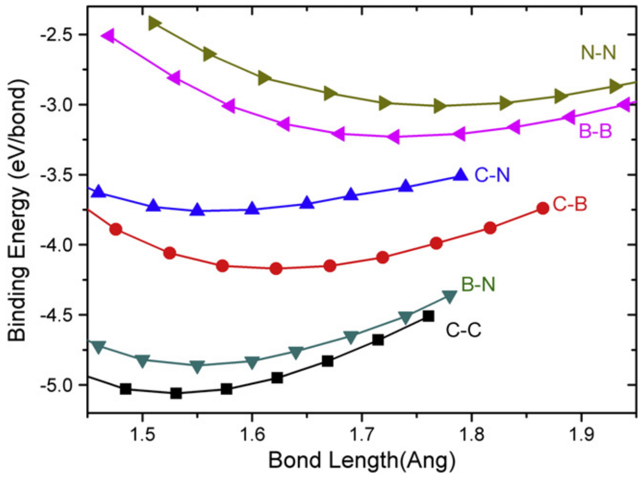

Fig. 2. The binding energy of various bonds versus the bond length. The C–C bonds and B–N bonds are regarded as the good bonds, while the B–B bonds and N–N bonds are identified as the bad bonds.