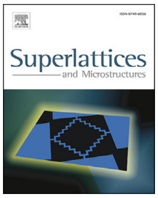
Superlattices and Microstructures 88 (2015) 371–376

Contents lists available at ScienceDirect

Superlattices and Microstructures

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



Absorption of NH_3 on pristine and defected boron nitride nanosheets: A first principle study

Hui Li[*], Zheng Chen, Xiaoliang Fang, Deyou Tie

State Key Laboratory of Solidification Processing, School of Material Science and Engineering, Northwestern Polytechnic University, 127 YouYi Western Road, Xi'an, Shaanxi, 710072, China

ARTICLE INFO

Article history:
Received 11 September 2015
Accepted 26 September 2015
Available online 12 October 2015

Keywords:
Boron nitride
First principle
Fictionalized
Defected

ABSTRACT

Versatile functional groups can be connected to Boron Nitride nanosheet (BNNS) through Lewis acid/base interaction for targeted applications. However, there have been few experimental reports about Lewis acid attack at the N atoms on BNNS, so far as we see. VdW-DFT is employed in this paper to investigate the interaction between NH_3 representing Lewis base and pristine or defected BNNS. Comparing the binding energy, separation and charge distribution of NH_3 and pristine or defected BNNS systems, the distinctive defect in BNNS is found to be the key role in the absorption progress. Thus, it is supposed that the missing of Lewis acid and BNNS complex can be attributed to the absence of N vacancies and B-edges in BNNS.

1. Introduction

Boron Nitride nanosheet (BNNS) shares the same honeycomb structure and similar bond length with graphene [1], while its large band gap, excellent chemical stability, high transparency and atomic flat nature make it an ideal substrate for a variety of functional groups to reach targeted applications [2–4].

Functionalized graphene has caught quiet a lot of attention in recent years, [5–7] while there is only limited reports about functionalized BNNS. That may be contributed to the excellent resistance against oxidation of BNNS [8]. In fact, a widely used method [9] to produce graphene consist of the initial oxidation of graphite to graphite oxide, followed by the subsequent mechanical/chemical or thermal exfoliation of graphite oxide to graphene oxide sheets, and their eventual reduction to graphene. In this way, functional groups can be attached to graphene in covalent way. When it comes to boron nitride, Hexagonal boron nitride (h-BN) and BNNS do not oxidize unless they are heated above 800 °C in air [8].

The locally polarized B—N bonds make the attachment between B atoms and electron sufficient groups (such as amines and phosphine) possible [10,11]. The amino groups of octadecylamine (ODA) and an amine-terminated oligomeric polyethylene glycol (PEG) have been attached to the B atoms on hexagonal Boron Nitride (h-BN) surface in a top-down method to produce BNNS. Such complexation is explained by Lewis acid/base interaction. Then, electrophilic attack at the N atoms on BNNS should be possible. However there has been no experimental report as far as we know.

The defects in BNNS behave some interesting characteristics. Vacancy defects are the most common defect type in BNNS. These defects often exhibit well-defined geometrical shapes (mostly triangles). It is interesting that almost all the triangles have the same orientation on one monolayer. This indicates that all these vacancies are of the same type (B or N). The

---

[*] Corresponding author.
E-mail address: lihui920913@outlook.com (H. Li).

http://dx.doi.org/10.1016/j.spmi.2015.09.035
0749-6036/

vacancies are further confirmed as missing B atoms, which left dominating zigzag N-edges [12,13]. Several hypothesizes [14–17] have been suggested to explain the dominating observance of B vacancies, while none of them is convincing enough.

Both theoretical [18,19] and experimental [11] reports have confirmed that defected BNNS behave more chimerical reactive than pristine one. Is there any kind of relation between the type of functional groups and defects in BNNS? It is suggested that the absence of B atoms, the former electron donor, may cause the adjacent N atoms to be electron deficient, which can be an easy target for the nucleophilic Lewis base. On the other hand the absence of B-edges can be an obstacle for the formation of Lewis acid and BNNS complexes.

Density functional theory (DFT) is applied in this paper to investigate the interaction between Lewis base and pristine or defected BNNS. To simplify the computational model, NH_3 is employed to represent Lewis base. There have been several theoretical reports [18–20] about molecule and BNNS system. However, none of them has taken the distinctive defect behaviour in BNNS into consideration. Bader charge analysis is employed to investigate charge difference.

2. Method and computational details

Density functional theory (DFT) was employed to calculate ground state energies and optimized geometries with a projector augmented wave (PAW) basis set as implemented in Vienna ab-initio simulation package (VASP) code. The absorption progress involves both gas phase molecule systems and condensed matter problems. In such progresses, nonlocal, long-ranged interactions, such as van der Waals (vdW) forces are influential. Thus, vdW-DF [21,22] is employed. By appropriate.selection of its underlying exchange functional, the accuracy of vdW-DF can be dramatically improved both for dispersion and hydrogen bonded complexes which is called optB88-vdW [23] method. The primary structure, BNNS with a NH_3 of different distance from the 4 × 4 BNNS unit cell and posture, was optimized in two steps. A 300 eV cutoff energy, 10^{-3} eV electronic self-consistency energy criterion and 0.3 eV/Å for force was applied in the first geometry optimization. The second step employed a 450 eV cutoff energy, 10^{-4} eV electronic self-consistency energy criterion and 0.05 eV/Å for force, while the k points in both steps was fixed as 5 × 5 × 1.

3. Results and discussion

To investigate the interaction between NH_3 molecule and BNNS (pristine or defected), the binding energy (E_b) was defined as:

$$E_b = E^{opt}_{NH_3+BNNS} - E^{8Å}_{NH_3+BNNS} \tag{1}$$

Where $E^{opt}_{NH_3+BNNS}$ denotes the total energy of the optimized NH_3 molecule and BNNS structure, while $E^{8Å}_{NH_3+BNNS}$ represents the total energy of BNNS with NH_3 molecule 8 Å from the BNNS atom plane, a distance large enough to ignore the interaction between BNNS and NH_3. The distance between BNNS and atom in NH_3 which is nearest to BNNS (D) was also investigated.

3.1. NH_3|pristine BNNS structures

For the absorption of NH_3 on pristine BNNS, different possible NH_3 locations were considered, including top of B atom (a), top of N atom (b), middle of B and N (c) and centre of the ring (d), as is shown in Fig. 1. The N—H bond in these cases didn't have specialized orientation. In all these cases, the nearest atom to BNNS was N with the rest three H atoms forming a plane parallel to the BNNS plane. To take this into consideration, another two models (e, f) were built and calculated. In model Fig. 1 e, N in NH_3 was on the top of B in BNNS, the same as Fig. 1 a, while the projection of N—H bond on BNNS plane has the same orientation as B—N bond. The only difference between Fig. 1 e and Fig. 1 f was that NH_3 is turned upside down in Fig. 1 f.

The results of optimized structures are shown in Table 1. As we can see that the most stable absorption location is Fig. 1 e with an E_b of −0.168eV. The best NH_3 location seems to be the top of B atom. The little difference between the E_b of Fig. 1 a and Fig. 1 e confirms that the orientation of N—H bond doesn't have much affection on the absorption of NH_3 and pristine BNNS. Compared with Fig. 1 f, the lower E_b of Fig. 1 e demonstrates that N is preferable to the BNNS rather than H. All these can be well explained by the Lewis acid—base interaction. The electron deficient B atom in BNNS is an easy target for the electron sufficient N atom in NH_3.

It is noticed that the value of force criterion (EIDFFG) can make a big difference. Usually, in an optimized structure, BNNS with NH_3 nearest to it has the lowest free energy. For example, E_b of pristine BNNS and NH_3 on top of B atom with different D is shown in Fig. 2. The smallest D depends on the value of EDIFFG, in most cases. The larger EDIFFG you set, the smaller D the optimized structure behaves and the lower free energy you get. In another words, with reducing D, the biggest force on atoms increases while the free energy of the whole system decreases. The final result seems to be some kind of balance between energy and force.

3.2. NH_3|defected BNNS structures

Defects in BNNS usually behave well-defined geometry, mostly triangles. Zigzag N-edges are of dominating observance. An N+3B hole was employed here to represent defects in BNNS. Several investigated structures are shown in Fig. 3. NH_3 was