Computational Materials Science 142 (2018) 82–88

Contents lists available at ScienceDirect

Computational Materials Science

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

Displacement thresholds and knock-on cross sections for hydrogenated h-BN monolayers

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ARTICLE INFO

Article history:
Received 10 June 2017
Received in revised form 23 August 2017
Accepted 1 October 2017

Keywords:
Molecular dynamics
Displacement threshold energy
Radiation damage
Nanomaterials

ABSTRACT

In the present article, the authors initially studied the effects of hydrogenation on the displacement threshold energies (E_d) of B and N atoms in h-BN nanosheets with the help of reaction force field (ReaxFF) based molecular dynamics simulations. Subsequently, the E_d values estimated for B, N and H atoms were used for predicting the knock-on cross section for these atoms against electron irradiation. The results show that in most of the cases the displacement threshold value deteriorates with hydrogenation. The redistribution of charge among different atoms with the increase in B-N bond length plays a significant role in deciding the displacement thresholds for B and N atoms. It was predicted with the help of obtained E_d values that in a lower energy range the H atoms have a higher knock-on cross-section than B and N atoms against electron irradiation. The results from this study lead the authors to recommend cautious use of transmission electron microscopy for the characterization of hydrogenated h-BN nanosheets.

1. Introduction

Two-dimensional (2D) materials are arising as a new class of materials due to their unique properties [1–7]. Due to exceptional properties, graphene and hexagonal boron nitride nanosheets (h-BN) are the focus of current research in the field of nanofillers [5–7]. Due to the close resemblance in their atomic structures, graphene and h-BN nanosheets [6–9] have comparable mechanical and thermal properties [10]. Due to a high band gap in the range of ~5 eV, h-BN nanosheets exhibit electrically insulating behavior, which is in contrast to the semi-metallic to the metallic behavior exhibited by graphene. Higher thermal stability at extreme temperatures [11] in conjunction with electrically insulating properties make h-BN nanosheets an attractive candidate material for specific applications such as electronic packaging [12,13] and nano-devices [14,15]. h-BN has also been explored for developing applications in the field of biotechnology [16–18], nano and biosensors [19], and corrosion-resistant and thermally stable composites [20,21].

In recent years, hydrogen functionalization of 2D nanomaterials has been studied rigorously by researchers to tailor their properties and make them suitable for a variety of applications [22–26]. Hydrogen storage and generation [27–29], and applications in space programs [30–32] are emerging as promising fields for the application of h-BN nanofillers. In the context of hydrogen containment, the safe, economical and stable storage of hydrogen at room temperature is still a challenging task. h-BN nanofillers may also be valuable for space program technology based on a recent report released by NASA suggesting that materials containing hydrogen, boron, and nitrogen can provide improved radiation shielding [30]. A recent molecular dynamics based study by Kumar et al. [33] predicted a slight reduction in the overall mechanical strength of fully hydrogenated h-BN structures as compared to pristine h-BN. Schematic representations of pristine and hydrogenated h-BN structures are shown in Fig. 1. In contrast to fully hydrogenated and pristine h-BN structures, semi-hydrogenated structures of h-BN exhibit a substantial improvement in toughness, which opens new avenues for applications of h-BN nanofillers [33].

Researchers have extensively employed the displacement threshold energy (E_d) as a quantifying parameter to study the resistance of any material against radiation or neutron damage [34]. The displacement threshold energy signifies the minimum amount of kinetic energy required to depart an atom from its lattice position in a crystal. Zobelli et al. [35] employed density functional based tight binding calculations for predicting E_d values for boron (B) and nitrogen (N) in boron nitride nanotubes. Their calculations predicted nearly same E_d values of 15 eV and 14 eV for boron and nitrogen atoms, respectively. With the help of first principle molecular dynamics based simulations, Kotakoski et al. [36] estimated E_d values for B and N in a pristine h-BN nanosheet as 19.36 eV and

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https://doi.org/10.1016/j.commatsci.2017.10.001
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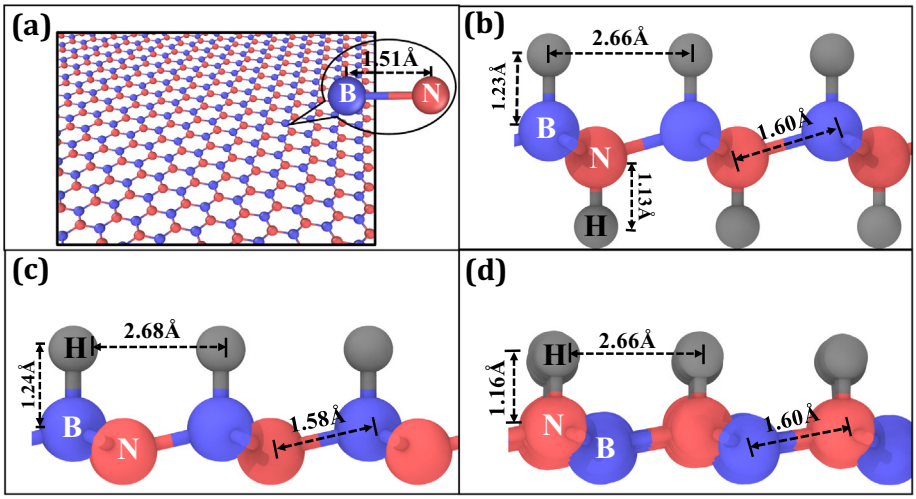

Fig. 1. Relaxed structures of (a) pristine h-BN (b) fully hydrogenated h-BN, and semi-hydrogenated h-BN with (c) H atom on boron only and (d) H atom on nitrogen only.

23.06 eV, respectively. The values reported by Kotakoski et al. [36] were higher than those estimated earlier by Zobelli et al. [35]. Kotakoski et al. [36] attributed the discrepancy with the values reported by Zobelli et al. [35] to an inadequate description of the charge transfer in the tight binding model used by Zobelli et al. [35]. Using static estimates, Kim et al. [37] also investigated the displacement threshold energy in h-BN nanosheets. They found E_d values for B and N atoms of 18.5 eV and 17.8 eV, respectively. It is apparent from the above literature that displacement threshold energy values as reported by different researchers using different modelling approaches differ slightly from each other. In addition to displacement threshold calculations, simulations were also performed by these authors [35,36] to estimate electron knock-on cross sections for boron nitride nanofillers to predict their interaction with electron radiation. A higher knock-on cross section usually indicates that the concerned material has a higher probability for interaction with incoming electron radiation. High-resolution transmission electron microscopy (HRTEM) and scanning transmission electron microscopy (STEM) are commonly used for mapping the localized atomic structure of nanofillers such as h-BN [37,38]. However, even a slightly higher electron beam energy than E_d may eject atoms from their positions and induce defects in the structure. Hence, to avoid atom ejection the electron beam energy requires fine tuning which also limits the application of these scanning techniques [38]. It is therefore important to study the effects of electron beam radiation on h-BN structures.

All previously reported studies were focused only on the pristine form of h-BN nanosheets, and none of those describes the effect of hydrogenation on the displacement threshold energy and electron knock-on cross section of h-BN nanosheets. The present authors herein pursued to investigate and quantify the effect of full and semi-hydrogenation on the resistance to electron irradiations of hydrogenated h-BN nanosheets.

It should be noted that hydrogenated structures of h-BN nanosheets are not fully covered with hydrogen, even in the fully hydrogenated structures. The chair type configuration (Fig. 1b) used in present simulations as the atomic configuration of h-BN nanosheets, still keeps B and N atoms exposed to radiation, as can be inferred from Fig. 1b. On the other hand, in semi-hydrogenated structures, hydrogen is only attached to either boron or nitrogen, which exposes one side of a sheet fully to radiations (Fig. 1c and d). Consequently, despite hydrogen providing a shielding, h-BN sheets remain vulnerable to radiation damage, and hence, studying the effect of hydrogenation on the displacement threshold energy and electron knock-on cross section is a necessary undertaking. Studying the electron knock-on cross section in conjunction with displacement threshold energy calculations for the hydrogenated structure of h-BN nanosheet will help in assessing the limitations of using HRTEM and STEM techniques with these nanostructures. By employing an approach based on a Primary Knock-on Atom (PKA), further insight into the probable interactions with electrons is provided.

2. Modelling method

A molecular dynamics based approach was adopted in this research work to study the effect of hydrogenation on the displacement threshold energy and electron knock-on cross section for h-BN nanosheets. Due to its straightforward and accurate parametrization, the Tersoff potential has become one of the most widely used methods for estimating the various properties of BN nanofillers [39–42]. However, in the present study, the reaction force field (ReaxFF) potential [43,44] was used for capturing interatomic interactions. Even though the ReaxFF potential is more computational intensive as compared to the Tersoff potential, the ReaxFF potential incorporates electrostatic charge distributions as well as bond breaking and bond formation. Also, while simulating radiation damage or neutron irradiation of atomistic structures the close encounter of nuclei will result in high repulsive electrostatic forces which can readily be captured with ReaxFF potential. The nonbonded electrostatic energy component in the ReaxFF potential facilitates the accounting for higher repulsive forces during the time of close atomic positions. In this article, ReaxFF parameters developed by Paupitz et al. [45] were employed for simulating the interatomic interaction between boron, nitrogen, and hydrogen atoms. In semi-hydrogenated structures of h-BN nanosheets, two separate atomic configurations were considered for the simulations, one with hydrogen attached only to boron, referred to as H-BN (Fig. 1c), and the other with hydrogen attached only to nitrogen atoms, referred as H-NB (Fig. 1d). Similarly, HBN refers to a fully-hydrogenated configuration in which hydrogen is attached to both boron and nitrogen (Fig. 1b). These three configurations have already been reported in the technical literature [29,46].

All the simulations reported in the present study were carried out using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [47] on an h-BN nanosheet with an approximate size of 100 Å by 102 Å with periodic boundary conditions imposed in all the principal directions. Field parameters of 6 Å and 4.5 Å were kept for the hydrogen bonding and nearest