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Self-Healing of Stone–Wales Defects in Boron Nitride Monolayer by Irradiation: *Ab Initio* Molecular Dynamics Simulations *

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We show an effective method of healing the Stone–Wales (SW) defects through low energy electron irradiation using ab initio molecular dynamics simulation. The SW defects can be healed by irradiation through bond rotation. Although the healing energy shows an anisotropic behavior, it is lower than the displacement threshold energy. The healing of the SW defect through electron irradiation can be effectively used in other sp^2-bonded materials.

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A hexagonal boron nitride (h-BN) layer has a two-dimensional structure similar to graphene with carbon atoms replaced by alternating boron and nitrogen atoms, and it exhibits a wide gap semiconductor due to ionic bonding between the atoms. Currently, h-BN represents an important new wide-band-gap nanomaterial with a theoretical band gap around 4.6 eV.[1] Also, h-BN possess some important advantages over graphene. An h-BN single layer has a wide range of attractive properties including high temperature stability, a low dielectric constant, high mechanical strength, and a large thermal conductivity,[2,3] leading to a number of potential applications in both structured and electronic materials. It is known that h-BN sheets are probably more resistant to oxidation and more suitable for high temperature applications where graphene would burn.[4] In particular, h-BN nanoribbons, i.e. a one-dimensional h-BN sheet, can present versatile electronic and magnetic properties depending on their edge structures, thereby holding great potential for nanoscale electronic and spintronic applications.[5–7] Various h-BN structures such as nanosheets and nanotubes have already been synthesized experimentally.[8,9] Recent studies have shown that h-BN can be used to improve the current voltage properties of graphene transistors by improving the mobility of electrons in graphene as compared to graphene films on silicon substrates.[10] These unique features make h-BN one of the most promising building blocks in nanotechnology applications. For example, the large band-gap and structural confinement have great potential use in technologies related to ultraviolet-blue light-emitting diodes, detectors, lasers, high temperature and/or high power devices, and potential spintronic devices.[11]

Similar to carbon-based nanostructures, h-BN based nanostructures are usually not defect free. Experimental observations showed that the B or N atoms could be removed under electron irradiation, leaving behind vacancies,[12,13] divacancies, or even extended topological defects.[14] In addition, the Stone–Wales (SW) defects were predicted to be formed in h-BN nanotubes under large tension.[15] These defects such as vacancies, anti-sites, pentagons, heptagons, dopants, and SW defects may impact the properties of h-BN based nanostructures and alter their electronic properties.[14–18] SW defects are very important in carbon- and h-BN-based nanostructures. Their presence has established unambiguously spectroscopic character in carbon nanotubes and BN nanotubes.[19] SW defects deform BN nanotubes severely and result in local curvature changes at defect sites.[20] All the fascinating properties of h-BN nanostructures relate to the defect-free case. However, defect formation is unenviable during device fabrication, so a successful route to heal the defects is needed. In this Letter, using *ab initio* molecular dynamics (MD) simulations we present a simple healing method of SW defects in h-BN by irradiation.

The calculations were based on first-principles density function theory (DFT), using the generalized gradient approximations, with the Perdew–Burke–Ernzerhof functional describing the exchange-correction function.[21] The DFT MD simulations were carried out using the SIESTA code,[22] which self-consistently solves the standard Kohn–Sham (KS) equations. An energy cutoff of 300 Ry is sufficient to converge the grid integration of the charge density. The interaction between the ionic cores and the valence electrons was modulated by norm conserving pseudopotentials.[23] The valence electron wave functions were expanded by using a double-ζ basis set plus polarization functions (DZP) and single-ζ basis set (SZ) function when calculating the defect formation

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energies and healing energies, respectively. The Brillouin zone was sampled by $(2 \times 2 \times 1)$ mesh points in the k space within the Monkhorst–Pack scheme.

All the calculations are based on the h-BN layer containing 224 boron and 224 nitrogen atoms, while the test calculations for a larger supercell with 1342 atoms (671 B+671 N atoms) show that the 448 atom supercell is large enough to ensure localization of point defects within the unit cell. Sufficient vacuum space (3.0 nm) is assigned along the direction perpendicular to the h-BN layer. The initial direction of a knock-on atom is represented by angles θ and ϕ as shown in Fig. 1. After giving a kinetic energy to an atom in the h-BN layer, the evolution of the system is involved using the *ab initio* molecular dynamics (MD) method for all the atoms, with a time step of 1.0 fs, and then, the system is further relaxed for 400 fs that is long enough for an escaping atom to return to its lattice site if no defect is created. All the simulations were initiated in the relaxed and undistorted h-BN layer structure at 0 K.

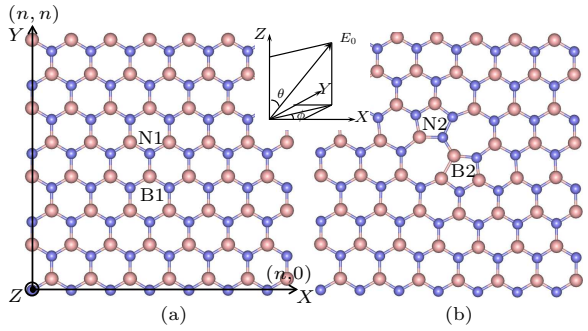


Fig. 1. Atomistic configuration of (a) a perfect h-BN layer and (b) the one with SW defects. The inset shows the notations used in the computation. The large and small balls represent the B and N atoms, respectively.

Figure 1 shows the notations and the physical model used in the present study. The Z axis is perpendicular to the layer of the graphene. The X and Y axes are along the $(n, 0)$ and (n, n) directions, respectively. The initial direction of a primary recoil atom (defined as the primary knock-on atom (PKA)) with an initial kinetic energy of E_0 is represented by angles θ and ϕ as shown in the inset of Fig. 1, where θ is the angle between the directions of PKA and Z axis, and ϕ is the angle between the X axis and the direction of PKA projected on the X–Y plane.

We first investigate the displacement threshold energy (T_d) of the h-BN layer. T_d is defined as the kinetic energy of the PKA that must have to leave its equilibrium site and cannot recover. For a crystal, this means the formation of a Frenkel pair, and the value of T_d is the minimum energy for such a defect to be stable against recombination. For the two-dimensional materials T_d means the minimum energy for the creation of unrecoverable defects. Table 1 lists the orientation dependence displacement threshold energy and the defects' type created by the irradiation. For the perfect h-BN layer, we obtain $T_d(\mathrm{B}) = 20$ eV and $T_d(\mathrm{N}) = 24$ eV along the Z axis, which agrees well with other calculations of $T_d(\mathrm{B}) = 19.36$ eV and $T_d(\mathrm{N}) = 23.06$ eV.[24]

Table 1. Angular dependence of T_d of the perfect h-BN layer.

PKA	θ (deg)	ϕ (deg)	T_d (eV)	Defect type
B1	0		20.0	Vacancy
B1	30	0	23.0	Vacancy
B1	45	0	21.0	Vacancy
B1	60	0	21.0	Vacancy
B1	30	30	21.0	Vacancy
B1	45	30	22.0	Vacancy
B1	60	30	21.0	Vacancy
N1	0		24.0	Vacancy
N1	30	0	24.0	Vacancy
N1	45	0	24.0	Vacancy
N1	60	0	23.0	Vacancy
N1	30	−30	24.0	Vacancy
N1	45	−30	22.0	Vacancy
N1	60	−30	22.0	Vacancy

Table 2. Changes of the healing energy as functions of θ and ϕ.

PKA	θ (deg)	ϕ(deg)	Healing energy (eV)
B2	30	30	13.0
B2	45	30	12.0
B2	60	30	12.0
B2	30	60	11.0
B2	45	60	11.0
B2	60	60	12.0
B2	30	90	14.0
B2	45	90	13.0
B2	60	90	13.0
B2	30	−150	15.0
B2	45	−150	13.0
B2	60	−150	13.0
N2	30	−150	7.0
N2	45	−150	8.0
N2	60	−150	8.0
N2	30	−120	6.0
N2	45	−120	7.0
N2	60	−120	8.0
N2	30	−90	8.0
N2	45	−90	8.0
N2	60	−90	9.0
N2	30	30	12.0
N2	45	30	11.0
N2	60	30	10.0

In order to avoid the generation of new defects through irradiation, initial kinetic energy E_0 lower than the minimum T_d value of 19 eV is tested in several directions to see whether the SW defects in the h-BN layer can be healed by low energy irradiation. Simulation results show that the SW defect can indeed be healed with low energy irradiation. The minimum healing energy as a function of θ and ϕ is shown in Table 2. It is clearly shown that the healing energy is smaller than the T_d, which means that SW defects can be healed through electron irradiation without the

formation of new defects. As only part of the healing energy transfers to the energy to overcome the rotation of B–N bonds, most of the healing energy will spread through lattice vibration to nearby atoms. This result will depend on the thermal conductivity of BN around the SW defects. Thus the healing energy shows anisotropic character, depending on the direction of the initial momentum of the atom, which ranges from 6 to 12 eV and from 11 to 15 eV for the N and B as the PKA, respectively.

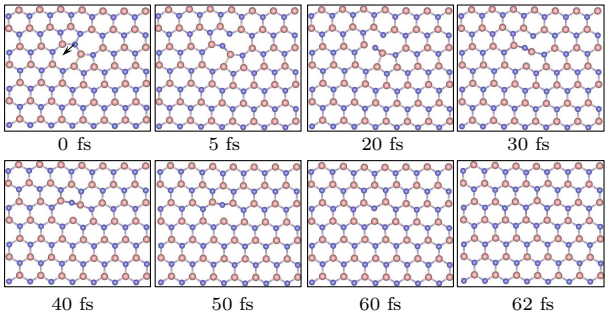


Fig. 2. Healing process of the Stone–Wales defect upon knock-on displacement with $\theta = 60°$, $\phi = -150°$ and $E_0 = 8.0$ eV with an N atom as the PKA.

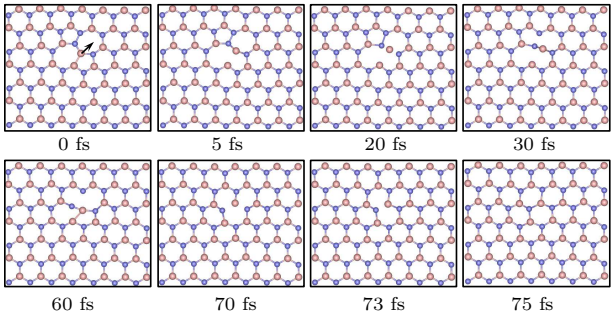


Fig. 3. Healing process of the Stone–Wales defect upon knock-on displacement with $\theta = 60°$, $\phi = 60°$ and $E_0 = 12.0$ eV with a B atom as the PKA.

Figure 2 shows a typical healing process with $\theta = 60°$, $\phi = -150°$ and $E_0 = 8.0$ eV with an N atom as the PKA. Starting from the SW defect, the N atom moves along the orientation of the initial momentum, the N–N bond breaks at 5 fs after the knock-on collision. The N atom moves along with further relaxation, the new N–B bond is formed at 40 fs, and finally the SW is healed at 62 fs. The healing process can be easily understood. To form an SW defect in the h-BN layer, an energy barrier should be overcome. As the energy of an SW defect in the h-BN layer is greater than that of a perfect one, a lower energy barrier needs to be overcome for the recovery of the SW defect, and the healing of SW of the electron energy is less than that of the formation of SW defects. The same healing process can be seen from the B atom as the PKA. Figure 3 shows the healing process with $\theta = 60°$, $\phi = 60°$ and $E_0 = 12.0$ eV with a B atom as the PKA.

The SW defects are formed by rotating a B–N bond by 90° in the hexagonal network of the h-BN layer; in this transformation four hexagons are changed into two heptagons and two pentagons. The in-plane rotation of B–N bond is investigated, i.e. with $\theta = 90°$. Figure 4(a) shows the energy as a function of the rotation angle of the B–N atom pair. The formation energy is about 7.2 eV, the top of the barrier is 9.0 eV above the perfect h-BN layer or 1.8 eV above the h-BN layer with the SW defect. This explains why only a small amount of energy is needed to heal the SW defect. By further rotating the B–N bond, an anti-site pair defect is formed; N and B atoms are replaced by B and N, respectively. For the higher energy barrier about 12.0 eV above the perfect h-BN layer, this defect has not been found experimentally. Although the energy barrier of the transformation of SW defects to a perfect BN lattice is only 1.8 eV, the minimum healing energy is about 6 eV. This is caused by the healing energy transfer to the kinetic energy of the PKA, which will spread through lattice vibration to the nearby atoms, and part of the energy is to overcome the energy barrier.

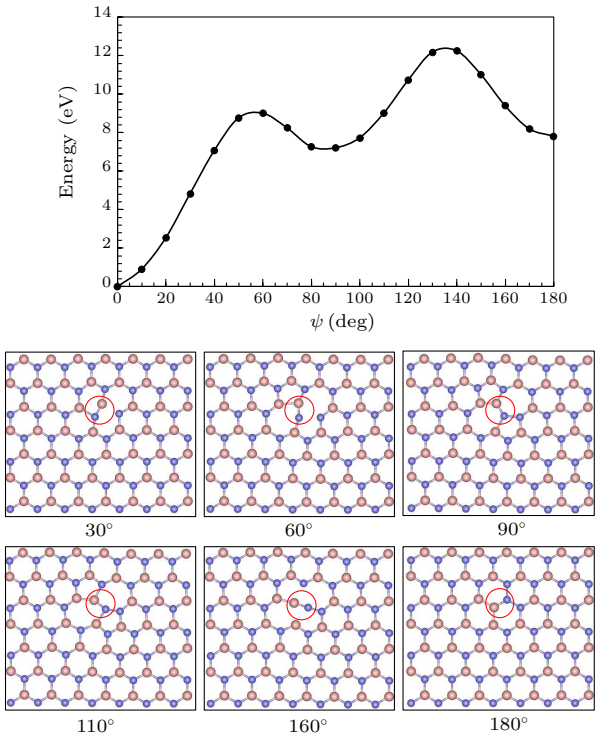


Fig. 4. Energy as a function of the rotation angle of the B–N atom pair and the atomic configuration of in-plane B–N atom pair rotation.

SW defects are very important factors that affect the properties of two-dimensional hexagonal structures.[25–29] SW defects have been predicted to alter the electronic properties of BN nanostructures, modify their chemical reactivity toward adsorbates, and likely impact upon their unique transport properties.[30–32] From the above results we can see

that the SW defects can be easily healed through irradiation without creating new defects. Thus irradiation can serve as a useful tool to modify morphology in a controllable manner, and to tailor the physical properties of a BN sheet with SW defects.

In summary, we have used *ab initio* molecular dynamics simulations to study the self-healing of SW defects in an *h*-BN layer. The SW defects can be easily healed through irradiation without new defect formation. The result presented here is helpful for the post healing the SW defects formed in sp^2-bonded layer characterization and device fabrication.

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