Vacancy migration in hexagonal boron nitride

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Activation energies and reaction paths for diffusion and nucleation of mono- and divacancy defects in hexagonal boron nitride layers are theoretically investigated. Migration paths are derived using the nudged elastic band method combined with density-functional-based techniques. We find a different behavior for migration of single boron and nitrogen vacancies with the existence of intermediate metastable states along the migration paths. The temperature dependence of entropic and vibrational contributions to the free Gibbs energies is explicitly taken in account. A rich phase diagram for vacancy migration is then obtained. Boron vacancies are first thermally activated and can migrate to form more stable BN divacancies. At high temperatures, the divacancies can further be activated. In the contrary, nitrogen vacancy migration is energetically unfavorable within all the temperature range below the melting point of h-BN.

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I. INTRODUCTION

Understanding the formation and diffusion mechanisms of point defects in layered structures is of fundamental interest due to the crucial role played by defects on electronic and mechanical properties of such systems.

Migration of vacancies in graphite has been the subject of a large number of experimental1–2 and theoretical3–5 studies, mostly motivated by the use of graphite as a neutron moderator in fission nuclear reactors. More recently, the interest on vacancy migration has been extended to carbon nanotubes.5 Recent developments in transmission electron microscopy techniques have shown the possibility of creating and imaging defects and monitoring in situ their evolution at room temperature3 and more elevated temperatures.7

Similarly to carbon, boron nitride (BN) occurs in a hexagonal layered phase (h-BN), as well as in nanotube and fullerene forms.8,9 Boron nitride based systems are also not defect free, and recently high-resolution electron microscopy has directly shown the in situ creation under electron irradiation of point and extended defective structures on single walled BN nanotubes.10 In the same study, strong vacancy binding energies were found, and it was shown how under irradiation this property promotes the formation of extended defects rather than a random distribution of individual point defects. By analogy to graphite, thermal vacancy migration and subsequent vacancy clustering can be seen as a competitive way to promote the appearance of extended defects. Individual vacancies in hexagonal boron nitride have electrically active gap levels,10,11 and thus it is also important to consider vacancy annealing processes to understand the evolution of this electrical activity with temperature.

In this context, a detailed description of migration paths and activation energy barriers is necessary for estimating vacancy diffusion coefficients and their temperature dependence. Knowledge of the total internal energy of the system is not sufficient to describe real thermal migration processes. Since a defective crystal is a grand canonical ensemble, a more appropriate thermodynamical function has to be considered, such as, for example, the Gibbs free energy, for comparison with experimental conditions. Temperature dependence of migration paths and activation barriers can then be taken into account, giving a more realistic picture of the migration processes.

Despite the structural similarity between carbon and boron nitride, the heteronuclear nature of boron nitride limits the transferability of what is known from carbon to this different compound. In spite of the large number of studies conducted on graphite,4,5 up to now, no studies of vacancy migration in layered BN systems have been reported. We present here a theoretical work on vacancy migration in hexagonal boron nitride sheets, considering single boron and nitrogen vacancies as well as divacancies.

We show different behaviors for single boron and nitrogen vacancies, where intermediate metastable states appear in the migration path. A complete phase diagram of migration processes is then described, which shows the importance of considering correct thermodynamical quantities in the estimation of migration barriers. For the monovacancies, the activation barriers are higher than in the equivalent case for graphite in all the range of temperatures considered, while the divacancy appears slightly more mobile than its graphite equivalent.

II. METHODOLOGY

We have considered for the perfect system a hexagonal 10 × 10 boron nitride supercell containing 200 atoms. Different sizes of the elementary cell were tested in order to minimize the interaction energy between defective structures in adjacent cells. Since we are only interested in defective structures in monolayers, the calculations have a single plane in the elementary cell and the c parameter of the lattice is large enough (12 Å) to avoid interlayer interactions.

Migration paths are derived using the nudged elastic band (NEB) technique12–14. In this method, a first chain of images \{R_s\} is built by linear interpolation of the initial and final configurations. Successively, all the intermediate images are
optimized simultaneously, where on each image \( R_i \) acts a force \( F_i \) expressed by

\[
F_i = -\mathbf{\nabla} V(R_i) + F_i^0
\]

where \( \mathbf{\nabla} V(R_i) \) is the component of the true force orthogonal to the path and \( F_i^0 \) is the component parallel to the path of an additional spring force connecting image \( R_i \) with the two contiguous images \( R_{i-1} \) and \( R_{i+1} \). This technique only requires structural information concerning the initial and final states, with optionally few other intermediate configurations. It is thus a suitable technique for exploring, in an efficient way, a large region of configuration space and deriving complicated minimum-energy paths. No a priori assumption for the migration path is required; in particular, there is no need to enforce symmetry at the saddle point.

Due to the slow convergence of the method, the use of standard density-functional-based techniques is too time consuming. The use of empirical techniques or force fields or classical potentials is not suitable due to their inability to describe phenomena far from equilibrium configurations for which parameters have been derived.

A good compromise between ab initio density-functional theory and classical empirical tight-binding methods can be obtained using density-functional tight-binding (DFTB) theory. This reduces computational time by some orders of magnitude while remaining a quantum method. It has already been shown that combining DFTB and NEB gives results comparable to other higher-end techniques.

In our study, we have used parameters developed for boron nitride, already applied several times to solid-state BN and molecular systems and known to give a realistic description of energetics and structure. DFTB calculations have been performed using the DEMON2K code.

In order to correctly describe the migration path, we have used a high number of intermediate images in the NEB (from 20 to 50). After derivation of the minimum-energy path, a more accurate value of the total energy for each point of the path was obtained by a single point density-functional theory calculation in the local-density approximation (DFT-LDA) as implemented in the AIMPRO code. Atom centered Gaussians (four per atom) are used for the wave-function basis, each multiplied by spherical harmonics up to a maximum angular momentum of \( l=1 \). For the Gaussian with the second smallest exponent, the maximum is \( l=2 \).

Defective crystals are a great canonical ensemble. The correct quantity for comparison with experiment is not the total internal energy of the system but the Gibbs free energy:

\[
G = U - TS + \mu_i N_i
\]

where the total energy \( U \) of the system is the sum of the internal energy \( U_{\text{int}} \) and the vibrational energy \( U_{\text{vib}} \). The second term of the sum is the entropy \( S \) contribution to the free energy. The third term depends on pressure \( p \) and volume \( V \) and is commonly neglected, since usually the system is considered at constant volume and pressure. The last term depends on the number of particles \( N \) and their chemical potential \( \mu \) and only has an influence when the number of particles changes.

For the calculation of vibrational energy and vibrational entropy terms, we have considered a Boltzmann distribution of harmonic oscillators, which has been shown to give realistic results in the case of defect vibrational entropies. Vibrational energy can then be written as

\[
U_{\text{vib}} = \sum_{i=1}^{3N} \left( \frac{\hbar \omega_i}{\exp(\hbar \omega_i/k_BT) - 1} + \frac{1}{2} \hbar \omega_i \right)
\]

where \( \omega_i \) are the eigenfrequencies derived from the vibrational spectra of the defective structure, \( N \) is the number of atoms of the system, and \( T \) is the absolute temperature. Under the same hypothesis, the entropic term is

\[
S_{\text{vib}} = k_B \sum_{i=1}^{3N} \left( \frac{\hbar \omega_i}{k_B T} \right)^\frac{1}{2} \left( \frac{\hbar \omega_i}{k_B T} - 1 \right)^{-1}
\]

In this work we have derived the eigenfrequencies by diagonalization of the full dynamical matrix. The dynamical matrix is calculated numerically by means of finite differences of the forces. Since this task is extremely time consuming, the use of standard DFT techniques is usually limited to a small cluster of atoms close to the vacancy, but this approach can reduce the accuracy of the derived thermodynamic quantities. The use of DFTB allows the construction of the Hessian for the full system and it has been demonstrated to give results in good agreement with DFT calculations.

### III. RESULTS AND DISCUSSION

#### A. Vacancy migration paths

The vacancy in graphite induces a Jahn-Teller distortion, forming a weak C-C bond between two of the vacancy neighbors. Vacancy migration occurs through the displacement of one of the first neighboring atoms into the vacant site. The associated activation energy has been experimentally observed and theoretically estimated to be 1.4–1.8 eV.

As already mentioned, vacancies in boron nitride show important differences due to the heteronuclear nature of boron nitride. Homonuclear B-B and N-N bonds are energetically unfavorable, and both the single boron and nitrogen vacancies conserve the three fold \( D_{3h} \) symmetry around the missing atom without local reconstruction of dangling bonds. Just a small relaxation of the three neighboring atoms surrounding the vacancy occurs, inward for the B atoms surrounding the N vacancy and outward for the N atoms surrounding the B vacancy. Formation energies are also, respectively, 11.22 eV for a boron vacancy and 8.91 eV for a nitrogen vacancy.

In Fig. 1, we have numbered the atoms of a h-BN sheet in order to have an accurate identification, in the text, of atoms involved during the migration processes.
cupy the vacancy site left by atom 1. In a boron vacancy migration process, atom 5 moves to occupy the vacancy site left by atom 1 (red arrow). The same process occurs for a nitrogen vacancy migration (yellow arrow).

We report in Table I a summary of the zero Kelvin activation barriers for the different types of defects considered obtained by DFTB and DFT. The agreement between the two series of values validates the DFTB approximation adopted in the NEB procedure. In the following text and graphs, we will refer to the more accurate results obtained by the successive DFT single point calculation.

We consider first a boron vacancy at site 1 of Fig. 1. The motion analogous to vacancy migration in graphite would be for a neighboring nitrogen atom (2, 3, or 4) to occupy the vacancy site 1. In boron nitride, this results in a N-antisite defect with two homonuclear N-N bonds. Density-functional calculation shows that such a structure is not stable and spontaneously relaxes back to the initial boron vacancy. A similar result is obtained for the nitrogen vacancy; it is clear that the mechanism for vacancy migration in graphite cannot be extended to boron nitride.

The correct boron-nitrogen atom alternation can be conserved, and a final configuration topologically equivalent to the initial one is obtained if migration occurs through the displacement of a second neighbor atom to the vacancy. The mechanism is illustrated in Fig. 1 by the red arrow, where boron atom 5 moves to the empty site left by atom 1. Relaxed structures with the vacancy at sites 1 and 5 have been used as initial and final images in the NEB calculations, respectively.

| TABLE I. Comparison of the zero Kelvin activation barriers for different types of defects calculated by DFTB and DFT. |
|---|---|---|
| | DFTB (eV) | DFT (eV) |
| B vacancy | 3.3 | 2.6 |
| N vacancy | 6.1 | 5.8 |
| BN divacancy: B moves | 4.9 | 6.0 |
| BN divacancy: N moves | 3.0 | 4.5 |

Figure 2 shows that boron vacancy migration is a multi-step process passing through intermediate metastable states. During the first step [Fig. 2(b)], the bond between atoms 5 and 6 is broken, and the nitrogen atom 2 forms a homonuclear bond with atom 3. This process corresponds to a barrier of 2.6 eV. The system then falls into a metastable configuration where atom 5 bonds with atom 4 and a nitrogen-nitrogen bond is reconstructed [Fig. 2(c)]. This configuration, 1.38 eV higher than the stable one, introduces non-hexagonal rings into the BN layer (a four, a five, and a seven membered ring). A new barrier of 0.72 eV occurs when the bond between nitrogen atoms 2 and 3 is broken [Fig. 2(d)]. The path then repeats symmetrically [configuration of Fig. 2(e) equivalent to that one of Fig. 2(c)] until the new stable configuration is reached [Fig. 2(f)].

Nitrogen vacancy migration follows a path equivalent to that illustrated for the boron vacancy, with structurally analogous intermediate metastable states (Fig. 3). Metastable states appear due to the reconstruction of a B-B bond; these are less energetically favorable than the corresponding states for the boron vacancy. Unlike the boron vacancy, the highest-energy configuration does not correspond to the initial bond breaking [Fig. 3(b)] moving into the first metastable state [Fig. 3(c)], but instead to the barrier connecting the two metastable configurations. The effective migration barrier corresponds to an energy of 5.8 eV, much higher than that of boron vacancies.

In a previous work, we demonstrated the existence of a strong binding force between BN vacancy pairs due to the strong electrostatic interaction between the two oppositely...
charged centers. This interaction is maximized when vacancies exist in neighboring sites and tends to promote the appearance of divacancies under irradiation. In accordance with this result, electron paramagnetic resonance (EPR) experiments conducted on γ-ray irradiated h-BN (Ref. 27) and BN multiwalled nanotubes28 have shown an extremely low concentration of paramagnetic centers related to single nitrogen vacancies. In this context, divacancies are believed to be one of the most probable defects on h-BN based materials. Then, the thermal stability of divacancies is of particular interest to understand the evolution of irradiated BN materials.

In Fig. 4(a), we show the structure around a divacancy site relaxed by DFT. Unlike the monovacancies, the defect undergoes B-B and N-N limited bond reconstruction, resulting in two pentagonal and one octagonal rings. The two pentagonal rings are associated with one weak B-B bond of length 1.93 Å and a N-N bond of 1.74 Å.

We have tested several possible migration paths for the divacancy, the most favorable corresponding to the minimum number of bond breaking processes along the path. The mechanism is illustrated by the yellow arrow in Fig. 4(a). In the final configuration, Fig. 4(b), atom 1 moves to the center of the divacancy, the homonuclear bond between atoms 2 and 3 is broken, and both these two atoms bond with atom 1. A new pentagonal ring is then formed by reconstruction of the boron-boron bond between atoms 5 and 6. The final and initial structures, topologically equivalent, are related by a rotation of 30° perpendicular to the plane and a translation of 5.8 Å along a direction rotated by 30° with reference to the axis of the initial divacancy. An equivalent migration mechanism occurs when one of the two boron atoms of the second pentagon moves to the center of the divacancy and bonds with the two nitrogen atoms of the opposite pentagonal ring.

In Fig. 4, we show the energies of the minimum-energy path for these two cases. Both curves exhibit a single saddle point, so unlike the monovacancies, divacancy migration is thus a single step process. The migration barrier obtained when moving the nitrogen atom is 4.5 eV, significantly lower than the 6.0 eV barrier obtained when moving the boron atom. The energy difference is explained considering the bond breaking processes, which occur during the migration. In both cases, two heteronuclear B-N bonds and one homonuclear bond are broken, but moving the nitrogen atom breaks the B-B homonuclear bond, whereas moving the boron atom breaks the more energetically strong N-N bond.

**B. Activation barriers and Gibbs free energies**

The energies reported above correspond to the 0 K temperature barriers, since the contribution of the entropic term and the vibrational energy to the Gibbs free energy were not taken into account. Gibbs free energies $G$ have to be corrected by calculating vibrational energy and the entropic term as given in Eqs. (3) and (4). Along the migration path, nonequivalent structures have different vibrational spectra and, consequently, a different free-energy temperature dependence. Considering explicitly the temperature dependence of the activation barriers $\Delta G$ gives a more physical picture of the vacancy migration phase diagram in boron nitride.

In the case of a boron vacancy, we observe an interesting effect. The free-energy difference between the ground state [Fig. 2(a)] and the first saddle point [Fig. 2(b)] slightly decreases as a function of the temperature (Fig. 5, curve i), passing from 2.6 eV at 0 K to 2.25 eV at 1200 K. At the same time, the entropy has a stabilizing effect on the ground-
Vacancy migration is driven by thermal stochastic excitations. In this context, diffusivity $D$ can be derived considering a simple Arrhenius formula,

$$D = D_0 e^{-\Delta G(T)/k_B T},$$

where $\Delta G$ is the temperature-dependent activation energy. The diffusion coefficient $D_0$ can be estimated by

$$D_0 = \frac{d^2 \omega}{2},$$

where $d$ is the distance between the initial and final positions of the vacancy and $\omega$ is the migration attempt frequency, usually approximated by the Debye frequency of the system. In our systems, the distance $d$ is that between the centers of two adjacent hexagonal rings, 5.8 Å. For h-BN, we have calculated by DFT-LDA the highest vibrational mode to lie at 1340 cm$^{-1}$, corresponding to a Debye frequency of 4.02 × 10$^{13}$ s$^{-1}$.

The diffusion coefficients obtained for the migration processes described previously are plotted in Fig. 6. For the boron vacancy migration (curve i in Fig. 6), we have considered the highest saddle point at any temperature; point A represents the switch in the highest saddle point. Curve ii is the diffusion coefficient for a divacancy moving a nitrogen atom (corresponding to curve iii of Fig. 5). For all the range of temperatures considered in the graph, the nitrogen diffusion coefficient is below 10$^{-10}$ Å$^2$/s and so is not included here.

A rich phase diagram for vacancy migration can now be described. Up to 840 K, all the diffusion coefficient are lower than 1 Å$^2$/s, and migration induced by thermal stochastic excitations cannot occur within the characteristic

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**FIG. 5.** Temperature dependence of the migration activation barrier for a boron vacancy (i for Fig. 2(b) and ii for Fig. 2(d)), nitrogen vacancy (v for Fig. 3(b) and vi for Fig. 3(d)), and BN divacancy (iii moving the nitrogen atom and iv moving the boron atom). The bold lines represent the effective migration barriers for the different vacancies.

**FIG. 6.** Temperature dependence of diffusion coefficient (i) for a boron vacancy and (ii) for a BN divacancy. The discontinuity at A corresponds to the switch in highest saddle point as shown in Fig. 5. The nitrogen vacancy diffusion coefficient has values lower than 10$^{-10}$ Å$^2$/s in all the temperature range considered in the graph.

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state configuration in comparison with the second saddle point configuration [Fig. 2(d)]. The difference of the free energy between these two states increases with temperature, passing from 2.1 eV at 0 K to 2.7 eV at 1200 K [Fig. 5, curve ii]. Thus at 680 K (point A in Fig. 5), curves i and ii cross and the second saddle point becomes the highest-energy configuration along the migration path. In this way, we obtain a more complicated schema for the migration barrier as a function of the temperature: the activation energy decreases from 0 to 680 K reaching a minimum of 2.4 eV, and then increases again once above 680 K.

In the case of the nitrogen vacancy, the free-energy difference between the ground state and the two saddle points increases with temperature [Fig. 5, curve v for Fig. 3(b) and curve vi for Fig. 3(d)]. The activation barrier thus strongly increases with temperature from 5.8 eV at 0 K up to 8.6 at 1200 K.

In contrast, the migration of divacancies becomes more favorable with increasing temperature. The difference in migration barriers to motion via boron (Fig. 5, curve iii) or nitrogen (Fig. 5, curve iv) atom displacement reduces, becoming negligible at elevated temperatures.

Explicitly including the temperature dependence of the activation barrier gives a more correct description of the phase diagram for vacancy migration. At 0 K, nitrogen vacancies and BN divacancies only show a small difference in activation energies, but this difference strongly diverges with increasing temperature, resulting in a large difference in the migration probability as it will be discussed in the following section.
time of experiments and usual spot annealing conditions. Between 840 and 1400 K, boron vacancy diffusion coefficient is bigger than 1 Å²/s and boron vacancies can be assumed to be mobile. The strong electrostatic interaction with single nitrogen vacancies will tend to trap mobile boron vacancies, promoting the formation of BN divacancy species. The probability of migration of divacancies is low up to a temperature of 1400 K, at which migration can occur. The high migration barrier of N vacancies imply that migration cannot be thermally excited.

Thus, through a spot annealing between 840 and 1400 K, it is possible to reduce the number of monovacancies in a hexagonal BN layer, transforming them in divacancies through a mutual annihilation process of single boron and nitrogen vacancies. This will remove electrically active and EPR allowed levels associated with the monovacancy spectra species.

**IV. CONCLUSIONS**

In this paper, we have investigated the complex process of vacancy migration in hexagonal boron nitride. Despite the structural similarity between hexagonal boron nitride and graphite, the heteronuclear nature of BN is at the origin of fundamental differences between the two systems. Vacancy migration in graphite occurs through the motion of one of the first neighbors into the vacant site. However, in boron nitride, it is necessary to move a second neighbor atom in order to conserve the bonding alternation of the system.

Using a combined DFTB-NEB calculation method, detailed migration paths with intermediate metastable states have been derived for boron and nitrogen monovacancies and BN divacancies. Activation barrier and their temperature dependence have been derived explicitly by calculating the entropic and vibrational energy contribution on the Gibbs free energy.

We expect all vacancy species to remain immobile below 840 K, at which temperature boron can thermally migrate, likely trapping at nitrogen vacancy sites and removing their electrically active gap states. At 1400 K, BN divacancies will also become mobile; however, nitrogen vacancies do not undergo thermally activated motion below the melting point of h-BN. A similar picture cannot be derived just by a simple analysis of the 0 K migration barriers but needs a detailed description of temperature dependence of activation barriers.

Single walled boron nitride nanotube are structurally related to single hexagonal BN sheets; however, there is a qualitative structural difference between the monovacancy in the two systems. The curvature of the nanotube permits both for boron and nitrogen vacancy bond reconstruction between two atoms neighboring the vacancy, and this additional bond lies preferentially perpendicular to the tube axis. This effect has a tube size dependence and decrease with the increase of the tube radius.

In a similar way, the reconstruction due to a weak Jahn-Teller distortion for vacancies in graphite results much stronger in a single walled carbon nanotube due to curvature effects. Migration of single vacancies has been recently described on carbon nanotubes showing an anisotropic behavior of the migration mechanism and an increasing of migration barrier compared to graphite. A critical diameter of 25 Å has been found above which the system behaves as for graphite.

Migration in BN nanotubes should present a similar increase of migration barriers related to the bond reconstruction. The effect will be weaker on a nitrogen vacancy, for which a weak boron–boron bond reconstructs, than on a boron vacancy, where a more energetically favorable nitrogen–nitrogen bond appears. However, these additional homonuclear bonds are less strong than the equivalent additional carbon–carbon bond in carbon nanotubes. Therefore, the increase of migration barrier due to curvature effect should be less pronounced in boron nitride nanotubes than in carbon nanotubes and consequently the critical diameter smaller. We can then conclude that the above described migration mechanisms of vacancies in hexagonal boron nitride can be extended to the case of BN nanotubes with few modifications even for the most narrow tubes.

Similarly to vacancies, other processes, e.g., Stone-Wales rotations, are of critical importance in plastic deformation processes. Once again, if at first these processes could appear as similar for graphite and h-BN, they are certainly more complicated to generate in BN due to its heteronature. Correspondingly, mechanical response and thermal treatment of damaged h-BN will be significantly different from that of graphite.

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