Structure, energy, and structural transformations of graphene grain boundaries from atomistic simulations

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ABSTRACT
Domain/grain boundaries are often introduced into graphene during chemical vapor deposition growth processes. Here, we performed a series of hybrid molecular dynamics simulations to study the structures, energies, and structural transformations of symmetric tilt grain boundaries of graphene. The grain boundary comprises an array of edge dislocations, with the dislocation density increasing upon increasing the grain boundary misorientation angle. The dislocation in the zigzag-oriented grain boundary contains an edge-sharing pentagon/heptagon defect, whereas the dislocation in the armchair-oriented grain boundary contains two paired pentagon/heptagon defects. In some grain boundaries, out-of-plane buckling exists due to the presence of dislocations. In the transition region (the region between the zigzag- and armchair-oriented grain boundaries), the grain boundary structures feature complex mixtures of both zigzag and armchair grain boundaries. We also discuss the grain boundary transformations and migrations that occur upon adding or removing carbon atoms at the grain boundaries for all of our investigated types of grain boundaries.

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1. Introduction
Graphene, a two-dimensional (2D) material consisting of sp²-hybridized carbon atoms, has outstanding electronic, thermal, and mechanical properties [1–3], suggesting that it might play an important role in future electronic and nanoelectromechanical devices [4,5]. The methods for fabricating graphene films include mechanical exfoliation [6], thermal sublimation of silicon carbide [7], reduction of graphene oxide [8], and chemical vapor deposition (CVD) growth on polycrystalline Cu or Ni substrates using methane as the carbon source and Cu or Ni as catalysts [9,10]. Among these methods, CVD growth is probably the most promising because it allows the possibilities of fabricating low-cost, high-quality, and large-area graphene films. Nevertheless, impurities, dislocations, and grain boundaries are very likely to be introduced into graphene during the CVD growth process; these defects might change the material properties of graphene.

Scanning tunneling microscopy (STM) can be used to visualize defects in graphite [11–15]. Periodic arrays of protrusions, having heights of several angstroms, have been observed near the grain boundary regions [11,13,15]. An atomistic model of the graphite grain boundary has also been proposed, with the grain boundary consisting of a regular array of edge-sharing pentagon/heptagon (5/7) pairs [13]. The defects in graphene were first visualized after it had been subjected to electron beam irradiation; carbon adatoms, vacancies, divacancies, and point defect reconstructions were all been noted [16]. Recently, from CVD growth of graphene on a Ni (1 1 1) surface, Lahiri et al. reported that the graphene domain boundary between the face-centered cubic (FCC) domain (carbon atoms occupying FCC sites of Ni) and the hexagonal...
close-packed (HCP) domain (carbon atoms occupying HCP sites of Ni) might be metallic and might possibly be engineered to form conducting molecular wires [17]. Gao et al. also reported the existence of graphene domain/grain boundaries after CVD growth of graphene on Cu (1 1 1) [18]. The graphene grain boundaries they reported resemble a “stitched fabric” and are similar to previous observations of graphite grain boundaries. Furthermore, they also reported a decrease in the electron mobility of graphene that is caused by electron scattering at the grain boundaries [18]. In addition to potential impacts on electronic transport properties, graphene grain boundaries could also affect magnetic properties of graphene sheets. Recent magnetic force microscopy studies have revealed the presence of ferromagnetism at graphite grain boundaries [19]; subsequent theoretical calculations suggested that magnetic moments exist at graphene grain boundaries as well [20]. Thus, understanding the structures and dynamics of defect and their effects on the material properties of graphene will be necessary for the reliable fabrication of future graphene-based devices, and might provide new possibilities for manipulating the material properties of graphene.

A number of attempts have been made to investigate the defects and grain boundaries in graphene using theoretical calculations [21–26,28–30]. By employing first-principles calculations, the properties of — and the possibilities of engineering — several different types of defects, such as inverse Stone–Thrower–Wales defects, have been proposed [21,22]. The mechanical properties of graphene featuring Stone–Wales defects have been investigated using first-principles calculations [23]. Density-functional tight-binding calculations have been employed to study the structures, energies, and inflection angles of graphene grain boundaries [24]. Liu and Yakobson used finite-temperature-annealing molecular dynamics (MD) simulations to compute the graphene grain boundary structures and energies [25]. Yazyev and Louie investigated dislocations and grain boundaries in graphene based on dislocation theories [26]; they also calculated the grain boundary energies, by applying the Read–Shockley formula [27], and the grain boundary band structures [26]. Ariza and Ortiz employed the discrete dislocation theory to investigate the formation energies of graphene dislocations [28]; they found that the formation energies and structures they obtained resembled those from other models [29]. In addition to discrete dislocation theory, a topological continuum model has been developed to describe the formation energies of Stone–Wales defects in graphene [30]. In the present study, we performed a series of hybrid MD simulations, combining static relaxations and finite-temperature MD simulations [31], to investigate graphene grain boundaries. We systematically studied the structures and energies of symmetric tilt grain boundaries of graphene with a wide range of grain boundary misorientation angles. These grain boundaries comprise regular arrays of (57) pairs; some of them feature out-of-plane bucklings, consistent with previous observations [18]. We also computed the grain boundary energies of grain boundaries featuring various misorientation angles; we observed two cusps that had not been reported by Liu and Yakobson [25]. We also found, unexpectedly, that defects featuring out-of-plane bucklings can flip their directions of protrusion (we will report these “flipping defects” in detail in a future publication). In addition, we have investigated how these grain boundaries transfer from one configuration to another, or even migrate by adding/removing carbon atoms at the grain boundaries.

2. Simulation methods

In atomistic simulations, forming grain boundaries does not simply involve joining two grains together and then annealing the structure. The most stable graphene grain boundary must contain no dangling bonds. Therefore, to eliminate all dangling bonds and form a perfect sp²-hybridized bonding network at the graphene grain boundary, carbon atoms must be added or removed from the grain boundary. To fulfill this task, in this study we modified the hybrid MD simulation algorithm that has been employed for thin film deposition simulations [31]. The algorithm includes the following sequence of steps:

1. Divide the grain boundary region into hundreds of grids.
2. Deposit one probe atom from one of these grid points.
3. Relax the probe atom by using the conjugate gradient method; record the potential energy.
4. Repeat steps 2 and 3 for all grid points.
5. Deposit an adatom on the site that gives the lowest energy; run MD to anneal the grain boundary.
6. Repeat steps 2–5 until all dangling bonds have been eliminated at the grain boundary.

The simulation box was rectangular with the grain boundary parallel with the y direction. The simulation box size in the x direction was as large as possible to minimize finite size effects. Periodic boundary conditions were applied to both x and y directions; the simulation cell contained two grain boundaries to fulfill the periodic boundary conditions in the lateral dimensions. We employed the adaptive intermolecular reactive bond order (AIREBO) potential with long-range Lennard-Jones interaction [32] to describe the interactions between carbon atoms and the LAMMPS MD simulation package [33] to perform our hybrid MD simulations.

The grain boundary energy \( \gamma \) was computed using the following formula:

\[
\gamma = \frac{N(E_{\text{GB}} - E_{\text{graphene}})}{2L_{\text{GB}}},
\]

where \( N \) denotes the number of atoms in the system; \( L_{\text{GB}} \) refers to the length of the simulation cell of the system along the grain boundary direction (i.e. the y direction), a factor of two in the denominator is to account for the two grain boundaries in the simulation cell; \( E_{\text{GB}} \) and \( E_{\text{graphene}} \) refer to the potential energy per atom of the system with grain boundaries and that of the pristine graphene.

In order to test the reliability of the AIREBO potential, we performed a benchmark \( ab \) initio calculation of a 13.17° grain boundary (Fig. 1b) with smaller grain sizes (∼36 Å), and compared the grain boundary energy and buckling magnitude (e.g. Fig. 1f) from \( ab \) initio calculation with those from MD calculations using the AIREBO potential. The grain boundary ener-
gies were computed using Eq. (1). For \textit{ab} initio calculations, we employed periodic plane-wave density functional theory calculations using the Vienna \textit{ab} initio simulation package [34–37] with the projector-augmented wave potentials [38] and the PBE functional [39]; the energy cut-off was set to 400 eV and a $1 \times 4 \times 1$ k-point mesh was used. The geometry convergence criterian was set to $F_{\text{max}} < 0.01$ eV/Å, where $F_{\text{max}}$ is the maximum force acting on the mobile atoms. The grain boundary energies from \textit{ab} initio calculation and MD calculation are 0.479 and 0.414 eV/Å, respectively; the buckling magnitudes are 1.85 Å from \textit{ab} initio calculation and 1.46 Å from MD calculation. Thus, the agreements between \textit{ab} initio calculation and AIREBO potential MD are reasonable.

### 3. Grain boundary structures and energies

Fig. 1 displays the tilt boundaries in the zigzag-oriented graphene obtained from hybrid MD simulations with different misorientation angles in the zigzag orientation ($\theta_{\text{zigzag}}$). The grain boundaries comprised arrays of $5\bar{7}$ pairs. By plotting Burgers circuit around the $5\bar{7}$ pair in Fig. 1a, we find that each $5\bar{7}$ pair is an edge dislocation with a Burgers vector $b$ of $(1, 0)$. The Burgers vector $b$ is simply the linear combination of two unit vectors of graphene, $a_1$ and $a_2$; that is, $b = na_1 + ma_2$ ($a_1 = (3d/2, -d/2)$; $a_2 = (3d/2, d/2)$; where $d$ (1.42 Å) is the nearest neighbor distance between carbon atoms). From Fig. 1b–e, we find that as the misorientation angle increases, the spacing between neighboring $(1, 0)$ dislocations decreases, equivalent to an increase in dislocation density. One interesting observation from Fig. 1c and d is that the dislocation distributions are not uniform; in the 16.43° grain boundary (Fig. 1c), two $5\bar{7}$ pairs separated by one hexagon form a cluster; in the 17.90° grain boundary (Fig. 1d), three $5\bar{7}$ pairs separated by one hexagon form a cluster. In the 21.79° grain boundary (Fig. 1e), the separation between adjacent $(1, 0)$ dislocations is exactly one hexagon; therefore, the maximum misorientation angle for the zigzag-oriented grain boundaries is 21.79°. It is interesting that at smaller misorientation angles, $(1, 0)$ dislocations are not uniformly distributed. For example, in the 6.01° grain boundary (Fig. 1f), two $5\bar{7}$ pairs separated by one hexagon form a cluster. In the 13.17° grain boundary (Fig. 1b), the separation between adjacent $(1, 0)$ dislocations is exactly one hexagon; therefore, the maximum misorientation angle for the armchair-oriented grain boundaries is 13.18°. It is interesting that at smaller misorientation angles, $(1, 0)$ dislocations are not uniformly distributed. For example, in the 13.18° grain boundary (Fig. 2a), two $5\bar{7}$ pairs separated by one hexagon form a cluster.
locations induce out-of-plane bucklings (Fig. 1f). Thus, the grain boundary contains an array of out-of-plane bucklings.

Fig. 2 displays the results of our hybrid MD calculations of the tilt boundaries in armchair-oriented graphene. The grain boundary in the armchair orientation comprises a regular array of defects with two paired 5/7 defects. Fig. 2a reveals that this defect is also an edge dislocation with a Burgers vector \( \mathbf{b} \) of \((1, 0) + (0, 1)\). Once again, we observe in Fig. 2b–e that the dislocation density increases upon increasing the misorientation angle, with the spacing between two adjacent \((1, 0) + (0, 1)\) dislocations decreasing from three hexagons (Fig. 2b) to one hexagon (Fig. 2d). In the 27.79° grain boundary, no separation exists between neighboring \((1, 0) + (0, 1)\) dislocations (Fig. 2e). Thus, the misorientation angles of the armchair-ori-

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**Fig. 3** - Symmetric tilt grain boundary structures of the grain boundaries in the transition region, 21.79° < \( \theta_{\text{zigzag}} \) < 32.21°. (a) \( \theta_{\text{zigzag}} = 23.3° \); (b) \( \theta_{\text{zigzag}} = 24.43° \); (c) \( \theta_{\text{zigzag}} = 26.01° \); (d) \( \theta_{\text{zigzag}} = 27.79° \); (e) \( \theta_{\text{zigzag}} = 29.41° \); (f) \( \theta_{\text{zigzag}} = 30.16° \); (g) structure and Burgers vector \( \mathbf{b} \) of the \((1, 0) + (1, 0) + (1, 0)\) dislocation. The orange dashed line highlights the Burgers circuit. (For interpretation of the references in colour in this figure legend, the reader is referred to the web version of this article.)
ented grain boundaries are limited by a maximum value of 27.79°. Similar to the zigzag-oriented grain boundaries, in some of the armchair-oriented grain boundaries each \((1, 0) + (0, 1)\) dislocation also bulges out and introduces a periodic array of out-of-plane bucklings (Fig. 2f).

Note that the misorientation angles of the armchair-oriented grain boundaries \(\theta_{\text{armchair}}\) (Fig. 2) can be converted to the misorientation angles of the zigzag orientation \(\theta_{\text{zigzag}}\) (Fig. 1) through the equation

\[
\theta_{\text{armchair}} = 60° - \theta_{\text{zigzag}}. \tag{2}
\]

Thus, the corresponding values of \(\theta_{\text{zigzag}}\) of the armchair-oriented grain boundaries in Fig. 2 range from 32.21° (Fig. 2e) to 46.82° (Fig. 2a). Because the maximum misorientation angle of the zigzag-oriented grain boundary is 21.79°, there must exist a transition region with misorientation angles of the zigzag orientation \(\theta_{\text{zigzag}}\) ranging from 21.79 to 32.21°. Fig. 3 presents the grain boundary structures in the transition region. We observe that the grain boundary structures in the transition region are no longer regular arrays of single-type dislocations. Instead, the grain boundaries contain two different types of dislocations: the first type is the \((1, 0)\) dislocation; the second can be viewed as that obtained after squeezing three \((1, 0)\) dislocations together with a Burgers vector \(b\) of \((1, 0) + (1, 0) + (1, 0)\), as indicated in Fig. 3g. When the misorientation angle is close to that of the zigzag-oriented region \(\theta_{\text{zigzag}} < 21.79°\), the grain boundary contains more \((1, 0)\) dislocations and fewer \((1, 0) + (1, 0) + (1, 0)\) dislocations, as revealed in Fig. 3a and b. When the misorientation angle increases (from the zigzag orientation), however, the number of \((1, 0)\) dislocations decreases and the number of \((1, 0) + (1, 0) + (1, 0)\) dislocations increases. Finally, when the misorientation angle approaches that of the armchair-oriented region (Fig. 3d–f), no more \((1, 0)\) dislocations appear in the grain boundary region. If the misorientation angle continues increasing, the graphene lattice planes separating neighboring dislocations will vanish (Fig. 3f) and the structure will be exactly the same as that of the 27.79° grain boundary in Fig. 2e.

Fig. 4 presents the grain boundary energy \(\gamma\) as a function of the misorientation angle \(\theta\) of the grain boundary. \(\theta_{\text{zigzag}} = 0°\) \(\theta_{\text{armchair}} = 60°\) and \(60°\) \(\theta_{\text{armchair}} = 0°\) correspond to the pure zigzag- and armchair-oriented graphene sheets, respectively. For values of \(\theta_{\text{zigzag}}\) less than 21.79°, the grain boundary comprises \((1, 0)\) dislocations (Fig. 1); for values greater than 32.21°, the grain boundary comprises \((1, 0) + (0, 1)\) dislocations (Fig. 2). In addition, for values of \(\theta_{\text{zigzag}}\) greater than 32.21°, another type of grain boundary exists, where the grain boundaries comprise \((1, 1)\) dislocations (we address the structures and energies of \((1, 1)\) dislocations in the next section). In Fig. 4, we observe two cusps located at values of \(\theta_{\text{zigzag}}\) of 21.79° and 32.21°, corresponding to the grain boundary structures in Figs. 1e and 2e, respectively. Cusps in the grain boundary energy curve are usually related to high-symmetry grain boundaries. Close examination of the grain boundary structures of the two cusps in Fig. 4 reveals that the orientations for the grain boundaries having values of \(\theta_{\text{zigzag}}\) of 21.79° and 32.21° are \((4, 2)\) and \((3, 1)\), respectively. Therefore, both are grain boundaries of higher symmetry than those of the grain boundaries comprising \((1, 0)\) and \((1, 0) + (0, 1)\) dislocations.

The buckling magnitudes \(\Delta H\) of grain boundaries as the function of the misorientation angles in zigzag orientation \(\theta_{\text{zigzag}}\) investigated in the present study are shown in Fig. 5a. It is very interesting to notice that there are two cusps corresponding to zero buckling. Close examination of Fig. 5a reveals that these two cusps correspond to the two cusps in Fig. 4; furthermore, for \((1, 0)\) and \((1, 0) + (0, 1)\) dislocations, it seems that smaller misorientation angles result in larger buc-

![Fig. 4 – Grain boundary energies of grain boundaries featuring different types of dislocations and misorientation angles. The bottom x-axis represents the misorientation angle of the zigzag orientation, \(\theta_{\text{zigzag}}\) the top x-axis represents the misorientation angle of the armchair orientation, \(\theta_{\text{armchair}}\).](image-url)
In Fig. 5b, we plotted the buckling magnitude of (1, 0) and (1, 0) + (0, 1) dislocations with respect to the length of the simulation cell along the grain boundary direction $L_{GB}$. Since in this study there is only one period along the grain boundary in the simulation cell, $L_{GB}$ is inverse proportional to the grain boundary dislocation density (except for the transition region). From Fig. 5b it is clear that there exists a general trend between $L_{GB}$ and buckling magnitudes; that is, shorter $L_{GB}$ (i.e. higher dislocation density) leads to smaller buckling. The possible explanation is that, as neighboring grain boundary dislocations get closer and closer, the strain fields induced by these dislocations overlap and cancel with each other; therefore, the buckling magnitudes drop as dislocation density increases, and eventually become zero when the separation between neighboring grain boundary dislocations becomes minimal (e.g. Figs. 1e and 2e).

Fig. 5 – (a) the buckling magnitude $\Delta H$ with respect to misorientation angle in zigzag orientation $\theta_{\text{zigzag}}$; (b) $\Delta H$ as the function of $L_{GB}$, the length of the simulation cell along the grain boundary direction.

4. Structural transformations and migrations of graphene grain boundaries after adatom deposition

We were also interested in the evolution of grain boundary and dislocation structures upon the deposition of carbon atoms. It has been reported that grain boundaries can migrate as a result of incoming deposition flux [40,41]. By employing the hybrid MD method, we can add carbon adatoms at locations that provide the lowest adsorption energies. Then, through follow-up annealing, we can study how grain boundaries evolve during successive deposition processes.

Yazyev and Louie reported that two types of topological defects exist with the same misorientation angles in the armchair orientation: (1, 0) + (0, 1) and (1, 1) dislocations [26]. They also computed the grain boundary energies of grain bound-
aries having these two types of defects, but the relationship between these two different types of dislocation remains unknown. Fig. 6 displays the pathway – determined from our hybrid MD simulation – through which a (1, 0) + (0, 1) dislocation transforms into a (1, 1) dislocation by depositing two carbon adatoms. Fig. 6a presents the original (1, 0) + (0, 1) dislocation. In Fig. 6b, two carbon adatoms have been deposited on the two edges of the heptagon shared with two adjacent pentagon rings. These two adatoms form a new covalent bond and the dislocation transforms from the (1, 0) + (0, 1) dislocation to the (1, 1) type (Fig. 6c). Fig. 4 also displays the computed grain boundary energies of grain boundaries comprised of (1, 1) dislocations. We conclude that the grain boundary featuring (1, 1) dislocations has a higher grain boundary energy compared with that of the original (1, 0) + (0, 1) dislocations at the same misorientation angle. Note that the whole grain boundary transformation processes can be reversed, as long as two neighboring carbon atoms of the pentagon evaporate from the surface of graphene.

Ding et al. proposed the phenomenon of dislocation climbing, due to carbon atom evaporation, in CNTs [42]. From our present simulations, we observed the reverse process in graphene; that is, dislocation climbing in graphene due to deposition of carbon adatoms. Fig. 7 presents the process of one (1, 0) dislocation impinging into a (0, 1) dislocation upon the deposition of two carbon adatoms at the 17.9° grain boundary (armchair-oriented). In Fig. 7a, the grain boundary comprises one (1, 0) dislocation and one (0, 1) dislocation.

Fig. 6 – Dislocation transformation upon successive deposition of adatoms. (a) Original (1, 0) + (0, 1) dislocation; (b) two carbon adatoms (colored in red) deposited at two edges of the heptagon shared with pentagons; a new covalent bond is about to form (red dashed line); (c) final structure: (1, 1) dislocation. The orange dashed line in (c) highlights the Burgers circuit. The bottom panel of each figure provides a perspective view. (For interpretation of the references in colour in this figure legend, the reader is referred to the web version of this article.)
In Fig. 7b, two carbon adatoms are deposited on the two edges of the lower heptagon; one adatom is deposited on the edge shared with the pentagon and the other is deposited on the edge shared with a hexagon. After the formation of the covalent bond between the two newly deposited adatoms, the lower 5\mid7 pair in Fig. 7a climbs up and impinges into the other dislocation, forming a (1, 0) + (0, 1) dislocation (Fig. 7c). The grain boundary energy of the boundary in Fig. 7a is 0.536 eV/Å, a value that is higher than that of the (1, 0) + (0, 1) grain boundary. In addition, the graphene lattice also bulges up as a result of the deposition of the adatoms. Other than the armchair orientation, dislocation climbing can also occur in the zigzag-oriented grain boundaries. Fig. 8 displays the evolution of the zigzag-oriented grain boundary with a misorientation angle of 16.43° upon the deposition of carbon adatoms. Fig. 8a presents the original grain boundary structure. After depositing two carbon adatoms, the upper (1, 0) dislocation in Fig. 8a climbs down and impinges into the lower (1, 0) dislocation, forming a (1, 0) + (1, 0) dislocation (Fig. 8b). The grain boundary energy of the grain boundary with the (1, 0) + (1, 0) dislocation is 0.501 eV, a value that is higher than that of the original one.

Deposition of adatoms in graphene can lead to grain boundary migrations. Fig. 9a displays the original configuration of the zigzag-oriented grain boundary having a misorientation angle of 7.34°. In Fig. 9b, two carbon adatoms are deposited on the two edges of the heptagon and a new covalent bond is formed between the two newly deposited atoms.
Fig. 8 – Dislocation climbing upon adatom deposition in the zigzag-oriented graphene. (a) Original grain boundary structure; (b) final (1, 0) + (1, 0) dislocation after deposition of two adatoms. The 5|7 pair that climbs in (b) is colored pink in all figures; the red crosses in all figures highlight the original location of the moving 5|7 pair in (a); the blue arrow in (b) highlights the displacement vector of the upper 5|7 pair. The bottom panel of each figure provides a perspective view of the system. (For interpretation of the references in colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 9 – Grain boundary migration upon adatom deposition. (a) Original grain boundary structure; (b) two adatoms deposited at the edges of the heptagon; (c) the two deposited adatoms form a covalent bond and the grain boundary migrates. In all figures, blue dashed lines highlight the original location of the adatoms; the green dashed line highlights the final location of the grain boundary; red crosses highlight the original location of the (1, 0) dislocation. The blue arrow in (c) highlights the displacement vector of the 5|7 pair. (For interpretation of the references in colour in this figure legend, the reader is referred to the web version of this article.)
In Fig. 9c, the pentagon in Fig. 9a has transformed into a hexagon and the hexagon into a heptagon, due to the newly deposited adatoms, with the (1, 0) dislocation climbing accordingly by a distance of 2.42 Å. By comparing Fig. 9a and c, we conclude that the grain boundary migrated due to dislocation climbing. Graphene grain boundary migration due to the deposition of carbon atoms is consistent with observations from growth simulations of polycrystalline Ni films [40,41].

5. Discussion

We have obtained the atomic structures and corresponding grain boundary energies of tilt grain boundaries in graphene having misorientation angles ranging from 6.01 to 46.82°. Notably, the (1, 0) dislocations in the 16.43 and 17.90° grain boundaries (Fig. 1c and d) are not uniformly distributed. To form a uniform distribution of dislocations at large misorientation angles, the spacing between dislocations must be an integral number of lattice planes terminating at the grain boundary. Close examination of the grain boundary structures in Fig. 1 reveals that the 16.43 and 17.90° grain boundaries fail to satisfy this; therefore, the distributions of dislocations in these two grain boundaries are not uniform.

In our grain boundary structures, most of the dislocations at the grain boundaries introduce out-of-plane bucklings. Therefore, the grain boundary comprises a periodic array of bulges. Our simulations revealed that these bucklings can flip from “bulging up” to “bulging down” (Fig. 10). Such dislocation flips are not surprising because the configuration in Fig. 10b is simply the inversion of that in Fig. 10a; both configurations should have identical energies. We will further explore the properties of flipping topological defects in graphene in a future study. Another interesting feature of our present study is the validity of using the Read–Shockley formula [27] to estimate grain boundary energies in graphene. Notably, however, the existence of strain in the third dimension (z direction), due to out-of-plane bucklings near dislocations, might cause the plane-strain conditions required for the Read–Shockley formula to no longer be valid.

From simulations of the deposition of carbon adatoms, we found that adatoms prefer being deposited on the edges of heptagons, as indicated in Figs. 6b, 7b, and 9b. Fig. 11 presents the adsorption energy map for the adsorption of a carbon dimer on a (1, 0) + (0, 1) dislocation. It is clear that the most favorable site for carbon dimer deposition is site I, where the two carbon atoms are deposited on the two sides of a heptagon that are shared with two adjacent pentagon rings. The least favorable sites for carbon dimer deposition are the sides of hexagons. Thus, incoming carbon atoms prefer migrating toward the grain boundaries and depositing on the edges of heptagons. Because the diffusion barriers of carbon atoms on graphite (or graphene) are low and the growth temperatures are usually high [9,10], it should be easy for carbon atoms to find graphene grain boundaries and incorporate into them.

Dislocation transformations, climbing, and grain boundary migrations induced by adatoms depositing at the grain boundaries are very interesting phenomena that might have important implications in the evolution of graphene microstructures during CVD growth. Figs. 6–8 reveal that the same misorientation angle can lead to different types of grain boundary structures as a result of successive depositions of carbon atoms. In Fig. 4, the grain boundary energies of the grain boundaries comprising (1, 1) dislocations are higher than those comprising (1, 0) + (0, 1) dislocations. Despite the grain boundary energies of the (1, 1) dislocations being higher, it is highly likely that the original (1, 0) + (0, 1) dislocation will transform into a (1, 1) dislocation during the deposition process because the energy penalty for forming (1, 1) dislocations is lower than that for forming a small graphene island above the original graphene film. To justify this argument, we computed the formation energy of a (1, 1) dislocation and a graphene surface dimer (i.e. two-atom island) at the 27.8° grain boundary (armchair-oriented). The formation energy of a (1, 1) dislocation is 7.59 eV lower than that of a graphene surface dimer; this shows that forming a (1, 1) dislocation is ener-
getically more favorable than forming an island. When increasing numbers of carbon adatoms are incorporated into the grain boundaries, however, the grain boundary energy should increase accordingly, with the energy penalty for grain boundary transformation surpassing that for forming a small graphene island beyond a critical number of adatoms. A multilayer graphene film will then be formed because it is energetically more favorable. Thus, understanding the different factors affecting whether the extra carbon atoms are incorporated into different types of grain boundary or are used for the formation of graphene island will be crucial for controlling the morphologies of graphene films grown through CVD.

6. Conclusions

We have used a series of hybrid MD simulations to investigate the symmetric tilt grain boundaries in graphene. In zigzag-oriented graphene grain boundaries, the grain boundaries comprise edge-sharing pentagon/heptagon pairs, or (1, 0) dislocations; in the armchair-oriented grain boundaries, the grain boundaries comprise (1, 0) + (0, 1) dislocations; in the transition region, the grain boundaries comprise mixtures of both (1, 0) and (1, 0) + (1, 0) dislocations. We also computed the grain boundary energies to obtain grain boundary energy curves. We identified two cusps having misorientation angles ($\theta_{\text{zigzag}}$) of 21.79 and 32.21°. We also investigated the structural transformations of grain boundaries upon successive depositions of carbon adatoms. Greater numbers of carbon adatoms can be incorporated into the grain boundaries through grain boundary transformations. Furthermore, successive depositions of adatoms can lead to grain boundary migrations and dislocation climbing. By providing insight into the structures of grain boundaries in graphene over a wide range of misorientation angles, this study sheds light onto the evolution of microstructures of graphene films grown through CVD.

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