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Atomistic study on the strength of symmetric tilt grain boundaries in graphene

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Molecular dynamics (MD) simulations were employed to study the mechanical response of various bicrystal graphene consisting of symmetric tilt boundary subject to uniaxial tensile loading at room temperature. We found that the strength of zigzag-oriented graphene increases slightly with mis-orientation angle, while the strength of armchair-oriented graphene decreases slightly with mis-orientation angle. Given that the difference in strength is small, one might conclude that the dependence of strength of graphene sheet containing grain boundaries upon tilt mis-orientation angle is rather weak. The origin for such weak dependence is believed to be that these grain boundaries all consisting of pentagon-heptagon pairs do not resemble nano-cracks, which result in rather heterogeneous stress field around the crack tip and therefore stress gradient plays an important role. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4722786>]

Graphene, a two-dimensional monatomic thick building block of carbon allotropes (carbon nanotube, fullerene, diamond), has emerged as an exotic material of the upcoming century and attracted world-wide attention owing to its exceptional properties such as electronic,^{1,2} thermal,^{3,4} optical,⁵ and mechanical properties.⁶ Recent experiments have shown that the single layer graphene sheet synthesized by chemical vapor deposition (CVD) method ubiquitously contain grain boundaries, due to the fact that metallic foil serves as a nucleation site for individual grains of graphene.⁷ Although a number of studies^{8,9} have been conducted on the effects of various types of point defects on the mechanical properties of single crystalline graphene, the effects of grain boundaries on the mechanical properties of the polycrystalline graphene have been lacking.

Recently, using molecular dynamics (MD) simulations, Grantab *et al.*¹⁰ found that graphene sheets with large-angle tilt boundaries that have a high density of defects are much stronger than those with low-angle boundaries having fewer defects. Furthermore, they claimed that these non-perfect materials consisting of defects are as strong as the pristine graphene. However, we repeated the same simulations with the same potential within the same simulation package LAMMPS (Ref. 11), and we found that the results were in large discrepancy with what has been reported in the paper.¹⁰ On the contrary, an opposite tendency was observed for the zigzag-oriented graphene sheets.

The simulated bicrystal graphene were chosen, the same as in Ref. 10, except that we were not able to construct the 15.8° armchair-oriented graphene, and a 15.18° armchair-oriented graphene was studied instead. The detail of the grain boundary structures can be found elsewhere.⁴

The reactive empirical bond order (REBO) potential¹² was used for our MD simulations. The REBO potential has been shown to accurately capture the bond-bond interaction

between carbon atoms as well as bond breaking and bond reforming.¹³ When the fracture process is of interest, the interaction cutoff radius must be selected carefully to avoid the spuriously high force arising from improper cutoff radius. In this work, we set the cutoff radius to be the original value 2.0 Å as suggested in Ref. 14.

Our simulation models were all in the size of 16 nm × 16 nm. After the bicrystal graphene was constructed, the simulation cell was relaxed until little energy drift was observed. After reaching equilibrium configurations, the uniaxial loading was then applied in the following way: the two ends of graphene were fixed in the loading direction but were allowed to move in the lateral directions. Then one end was pulled in a constant velocity along the axial direction, which results in a constant engineering strain rate of 0.5 ps⁻¹.

The stress-strain curves of our studied bicrystal graphene are shown in Fig. 1. There are several appreciable differences between our results and what has been reported by Grantab *et al.*¹⁰

First, let us look at the fracture strain for each case. The observed differences in fracture strain between our results and Grantab *et al.*¹⁰ for all cases are more than 10%. For instance, our predicted fracture strain for 5.5° zigzag-oriented graphene was 0.32, while ~0.1 fracture strain was found in Grantab *et al.*¹⁰ Such huge difference cannot be attributed to the difference of simulation details. We notice that Grantab *et al.*¹⁰ used an arbitrary interaction cutoff 1.92 Å instead of 2.0 Å in the original REBO potential for C–C bonds without justification, which might be part reason of the discrepancy. To see if this is indeed the origin of discrepancy, we performed the simulations with cutoff of 1.92 Å. The comparison for 5.5° zigzag-oriented graphene is shown in Fig. 2, which shows that the difference in fracture strain is ~2%. Such small difference cannot fully capture the difference between ours and that in Grantab *et al.*¹⁰ It is worth noting that when dealing with stretching fracture of simulations for systems with voids or interfaces such as grain

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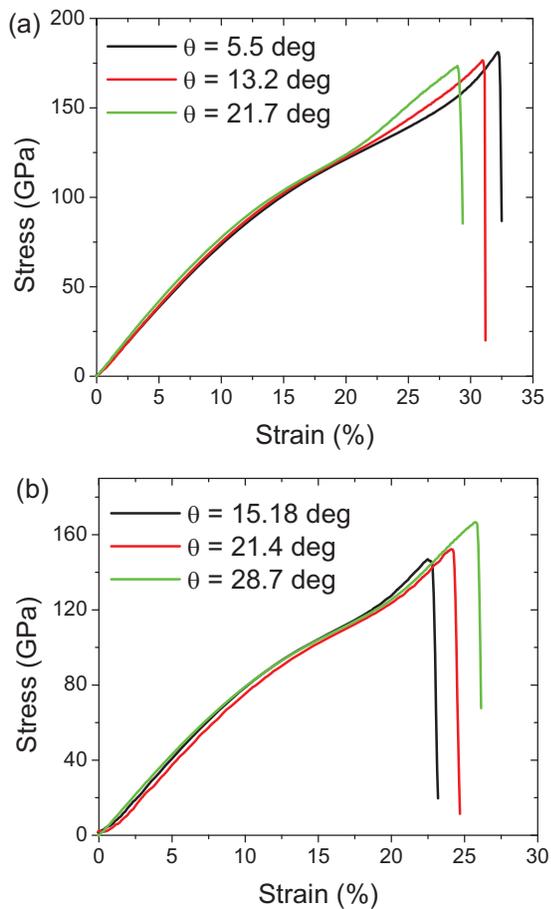


FIG. 1. The stress-strain curve for (a) zigzag-oriented, (b) armchair-oriented graphene, being pulled along direction perpendicular to the grain boundary. Note that we were not able to construct the 15.8° armchair-oriented graphene. A 15.18° armchair-oriented graphene was studied instead. Notice that the difference in fracture strength of all the two set of samples are unnoticeably small.

boundaries herein, the covalent interaction range should not be shorter than the original value 2.0 \AA . The shorter-range cutoff, especially at the boundary region, causes early fracture, and therefore the reduced fracture strains in their simulations are expected.

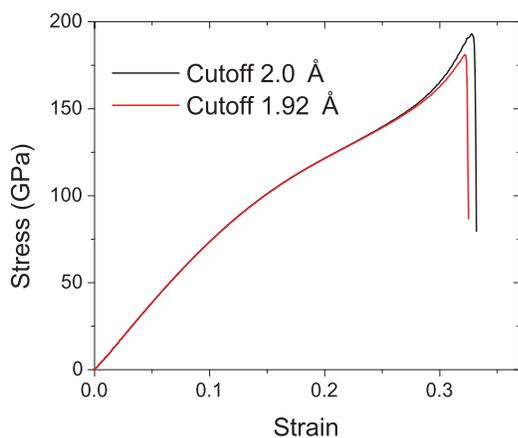


FIG. 2. The uniaxial tensile stress-strain curve for 5.5° zigzag-oriented graphene with cutoff of 2.0 and 1.92 \AA . The two curves overlap with each other and the difference between the two simulations of different inter-atomic potential cutoff is unnoticeable.

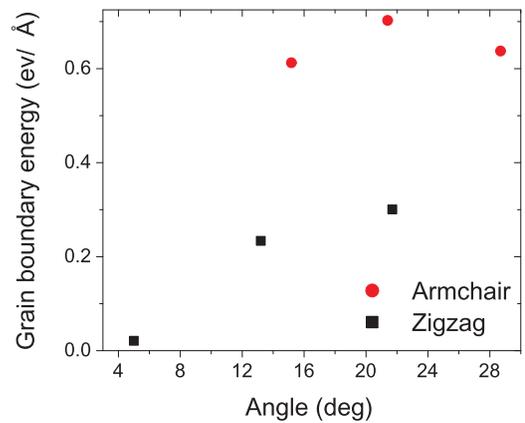


FIG. 3. The grain boundary energy as a function of tilt mis-orientation angle for both zigzag and armchair-oriented graphene.

Second, the trend that increase of strength with increasing the tilt angle, correspondingly the density of defects, is not observed in our simulated armchair-oriented graphene. In fact, the opposite tendency to Grantab *et al.*¹⁰ is observed. We also note that zigzag-oriented bicrystal graphene sheets have higher strength compared with armchair-oriented bicrystal graphene sheets, which is likely due to the different type of dislocations that form the grain boundaries. The $(1,0)$ type of dislocations are more favorable and have lower energy, compared with $(1,0)+(0,1)$ dislocation pair.¹⁵ The grain boundary energies of the simulated cases are shown in Fig. 3. The fact that armchair grain boundaries generally having higher energy than that of zigzag grain boundaries exhibit lower fracture strain/stress indicates the grain boundary energy is a good indicator for their tensile strength.

Third, we believe that the pentagon-heptagon pair, being the backbone of all the constructed tilt grain boundaries, is a little softer than the perfect hexagonal C lattice. The bicrystal graphene studied here, however, are different to the situation where finite-size cracks are present. This is because the stress field becomes quite heterogeneous when a crack is present, being dependent upon the distance to the crack tip. However, we find the atomic-level stress^{16,17} is heterogenous only in the grain boundary region whereas is quite uniform in the

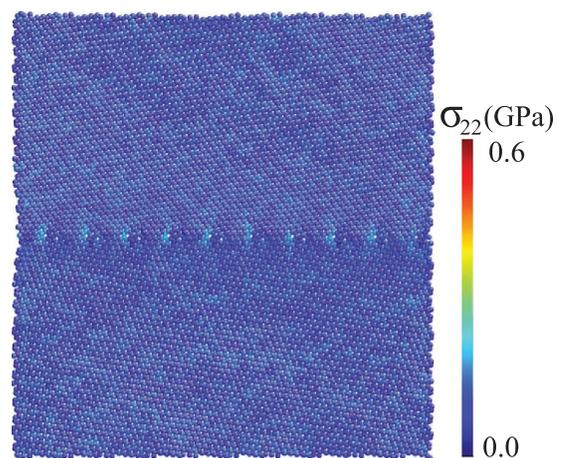


FIG. 4. The atomic-level stress characterization in the 15.18° armchair-oriented graphene at $\varepsilon=0$, showing the residual stress is heterogeneous at the grain boundary region while stress in the grain interior is quite uniform.

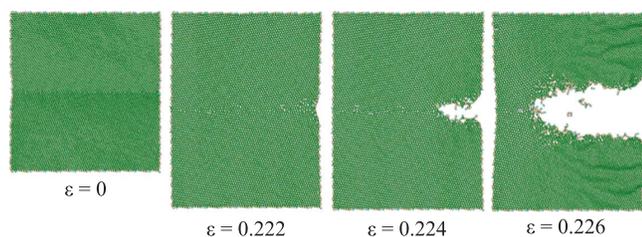


FIG. 5. The deformation snapshots showing the brittle failure in a 15.18° armchair-oriented graphene. The process consists of nucleating nano-crack at the grain boundary followed by quick growth of the crack. Atoms are colored by the coordination number. Green denotes atom with coordination number of 3 (perfect atoms) and other colors denote under-coordinated atoms.

grain interior (shown in Fig. 4). Such evidence reveals that the grain boundary differs fundamentally from nano-crack. In fact, starting from a bicrystal graphene with no presence of cracks, nucleation of nano-crack actually dominates the breaking point of the system. Shown in Fig. 5 is a representative brittle failure behavior of a 15.18° armchair-oriented graphene at various strains. Obviously, the junction between the right free surface and the grain boundary starts to shrink at strain of 0.222. At strain of 0.224, a small portion of bonds at right-side grain boundary breaks, which forms a nano-crack. Afterwards, the crack starts to propagate spontaneously, resulting in cleavage failure mode with no plasticity, corroborating the abrupt drop of stress once reaching the “maximum stress” (strength) as seen in the stress-strain curves in Fig. 1. This fundamentally differs from the classical fracture mechanics in the way that nucleation of nano-crack is the dominant physics dictating the failure of bicrystal graphene studied here.

Before closing, we would like point out that it is still premature to compare our theoretical results offered here with experimental studies due to the ideal grain boundary structures in our model in contrast with probably more complicated grain boundary structures in experimental samples. Specifically, triple junctions (TJs) in polycrystalline microstructures corresponding to one-dimensional regions of space where three grain boundaries meet are usually found in any

polycrystalline materials and, therefore, are expected to play an important role in the structure evolution and the overall mechanical properties. The modeling employing more realistic grain boundary structures is underway and will be presented in a near future publication.

In sum, MD simulations have been employed to study the mechanical response of various bicrystal graphene consists of symmetric tilt boundary subject to uniaxial tensile loading at room temperature. Based on the results of present study, we conclude that the dependence of strength of graphene sheet containing grain boundaries upon tilt grain boundary angle is rather weak.

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