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Anomalous Strength Characteristics of Tilt Grain Boundaries in Graphene

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Graphene in its pristine form is one of the strongest materials tested, but defects influence its strength. Using atomistic calculations, we find that, counter to standard reasoning, graphene sheets with large-angle tilt boundaries that have a high density of defects are as strong as the pristine material and, unexpectedly, are much stronger than those with low-angle boundaries having fewer defects. We show that this trend is not explained by continuum fracture models but can be understood by considering the critical bonds in the strained seven-membered carbon rings that lead to failure; the large-angle boundaries are stronger because they are able to better accommodate these strained rings. Our results provide guidelines for designing growth methods to obtain sheets with strengths close to that of pristine graphene.

Graphene is one of the thinnest materials ever synthesized, yet it is one of the strongest ever measured (1, 2), and it exhibits exceptional electronic, thermal, and optical properties (1, 3); however, growing large-area, single-layer graphene sheets remains a major challenge. Recently, a chemical vapor deposition (CVD) technique has been devised that exploits the low solubility of carbon in metals such as nickel (4, 5) and copper (6, 7) in order to grow graphene on metal foils. A consequence of this technique is that the large-area graphene sheets contain grain boundaries, because each grain in the metallic foil serves as a nucleation site for individual grains of graphene (6).

Tilt grain boundaries in graphite had first been observed in scanning tunneling microscopy (STM) experiments by Albrecht et al. (8), and since then several groups have performed similar microscopy studies (9–14). More recently, Hashimoto et al. (15) have observed individual dislocations in graphene using transmission electron microscopy (TEM), and the structure, as well as the electronic, magnetic, and dynamical properties of grain boundaries in graphene have been investigated by a number of other research teams (16–18). With all this previous work established, a natural question to ask is how these grain boundaries influence the mechanical properties of graphene. Given the fact that graphene is one of the stiffest (modulus ~ 1 TPa) and strongest (strength ~ 100 GPa) materials, in order to use CVD-synthesized graphene sheets in nano-electromechanical systems (NEMS), in sensors, and as pressure barriers, it is important to know how the grain boundaries influence these fundamental mechanical properties.

Although a number of studies have been carried out on the mechanics of dislocations and defects in carbon nanotubes (19–21) and graphene (22), the mechanical properties of hydrogen-functionalized graphene (23), and the fracture and failure of graphene and carbon nanotubes with multiple vacancies (24) and Stone-Wales defects (24–26), the effect of grain boundaries on the mechanical properties of graphene has been largely neglected. To address this outstanding problem, we have

Fig. 1. The structures of grain boundaries in (A to C) zigzag-oriented and (D to F) armchair-oriented graphene sheets with varying mismatch angles.
performed molecular dynamics (MD) and density functional theory (DFT) calculations using the packages Large-Scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) and Vienna Ab-Initio Simulation Package (VASP), respectively. The full details of the computational methods are included in the supporting online material (SOM).

The structures of tilt grain boundaries in zigzag- and armchair-oriented graphene are shown in Fig. 1 for various grain boundary angles (the angles represent the total mismatch angles between the left and right grains). For the zigzag orientation, the grain boundaries consist of repeating five- and seven-membered ring pairs (5–7 pairs) that are separated by several hexagonal rings (hex rings). As the grain boundary angle increases, the number of hex rings separating the 5–7 defects decreases, with the ultimate limit occurring at 21.7° when only a single hex ring separates the periodic 5–7 defects. Therefore, more severe grain boundary angles are composed of higher defect densities. The repeating defect pairs can also be thought of as an array of edge dislocations with horizontal Burgers vectors where the five-membered rings represent the extra plane of atoms, as shown in Fig. 1.

For the armchair orientation, the repeating defect consists of two diagonally opposed 5–7 pairs that are separated by several hex rings. As was the case for the zigzag orientation, larger grain boundary angles consist of higher defect densities; however, for the armchair-oriented graphene, the most severely misoriented boundary (28.7°) consists of repeating 5–7 pairs without any intermediate hex rings. Viewing the grain boundary in terms of dislocations, the two diagonally opposed, repeating 5–7 pairs represent two partial edge dislocations, as shown in Fig. 1. The vertical components of the Burgers vectors of the two partial dislocations nullify one another, leaving the grain boundary vertically oriented (for a vertical boundary, the net Burgers vector must be purely horizontal).

The stress-strain curves for zigzag- and armchair-oriented graphene sheets pulled perpendicular to the grain boundaries are shown in Fig. 2. In general, grain boundaries may be oriented at an angle relative to the tensile axes; to study the effect of this variation, we consider the extreme cases, that is, the grain boundaries oriented perpendicular to and along the loading axes. In both cases, the variation of the failure strength with angle is larger when the sheets are pulled perpendicular to the boundaries than when they are pulled parallel to the boundaries. From these plots, it can be seen that as the grain boundary angle, and hence the defect density, increase, the ultimate failure strength and strain at failure increase. These results are very unexpected and are completely contrary to the natural intuition that as the number of defects increases, the strength of a material decreases.

To see whether the nonintuitive results can be understood on the basis of continuum mechanics concepts, we consider a fracture-mechanics-based approach in which we model the seven-membered rings along the grain boundary as an infinite array of Griffith cracks. This is a reasonable continuum-level analog of the seven-membered rings, because these rings are larger than the hex rings and so they can be represented as a crack or a void within the material. This assumption is also consistent with the fact that failure in the graphene sheets always begins at the seven-membered rings. We therefore consider an infinite array of Griffith cracks (the crack tips aligned along the boundary), each of length 2a and separated by a length 2h from one another. The common method that is used to determine whether a crack advances upon application of a remote stress, σ, is to compute the stress-intensity factor, K. If K exceeds Kc (the experimentally measured fracture toughness for a given material), then crack propagation will ensue. The stress-intensity factor for the arrangement of cracks outlined above can be computed using standard fracture mechanics techniques (27) and is given by the following equation:

\[
K = \frac{\sigma \sqrt{2h a}}{2 \sqrt{\pi}}
\]

A plot of the non-dimensional stress-intensity factor, K/σ√a, versus normalized crack-spacing, h/a, is presented in Fig. 3. As the intercrack spacing, 2h, decreases, the stress-intensity factor, K, increases due to the interaction of the stress fields of adjacent cracks. Based on the plot in Fig. 3, graphene sheets should be weaker as the defect distribution becomes more dense. Clearly, this fracture mechanics analogy fails to explain our results, so the explanation we seek does not lie within continuum mechanics techniques but on the atomic-level details of bond rupture and failure. We therefore focus on the sequence of atomic-scale events that leads to tensile failure.

Figure 4 shows the first signs of failure within the zigzag- and armchair-oriented graphene sheets during deformation perpendicular to the grain boundaries. What is striking is that the first bonds to break (the encircled bonds) are always the same ones for all three grain boundary angles. The location of the critical bonds is dependent on the orientation of the graphene (zigzag or armchair) and the loading direction (perpendicular or parallel to the grain boundary); for each specific combination of orientation and loading direction, the critical bonds are the same for all three grain boundary angles. Once these bonds have been broken, complete failure of the sheets proceeds rapidly along the grain boundaries. There is, however, an exception in the case of the 28.7° armchair graphene, which actually fails away from the boundary, within the highlighted region in Fig. 4F.

The first signs of failure for the zigzag- and armchair-oriented graphene sheets pulled parallel to the grain boundaries are shown in Fig. S2. As was the case previously, we observe that for each of the three grain boundary angles, the same bonds in the seven-membered rings (the encircled bonds) are the first to break, although it should be reiterated that the critical bonds for this loading direction are different from those of the sheets that were pulled perpendicular to the boundaries. An exception arises again for the 28.7° armchair graphene, which fails away from the boundary.

Having identified the critical bonds, we now focus on the initial strains in these bonds as a function of the grain boundary angle and uncover clues toward understanding the anomalous strength

**Fig. 2.** The stress-strain curves of (left) zigzag-oriented and (right) armchair-oriented graphene sheets pulled perpendicular to the grain boundaries.

**Fig. 3.** Nondimensional stress-intensity factor versus normalized crack-spacing.
of tilt grain boundaries in graphene. As the grain boundary angle increases, the initial lengths of the critical bonds decrease toward the sp^2 carbon-carbon bond length in pristine graphene. Before any applied deformation, for loading perpendicular to the boundary, the strain in the critical bonds of the zigzag-oriented graphene sheets with grain boundary angles of 5.5°, 13.2°, and 21.7° are 12.2%, 10.3%, and 5.4%, respectively. Our DFT simulations validate these results and the general trend, with calculated strains of 9.5%, 8.7%, and 5.4% as the grain boundary angle increases. Naturally, as the prestrain in the material decreases, the strain at failure and ultimate strength will increase. It is the level of preexisting strain within the critical bonds of the seven-membered rings that accounts for the counterintuitive results we have observed in our simulations.

In the undeformed state, the critical bonds in armchair graphene pulled perpendicular to the boundary are strained by a factor of 23.4%, 9.3%, and 1.7% for the 15.8°, 21.4°, and 28.7° boundary angles, respectively. Once again, we observe the trend of decreasing initial strain with increasing grain boundary angle. Interestingly, the graphene sheet with a 28.7° grain boundary angle begins to fail away from the boundary at the location highlighted in Fig. 4F. This is because, in this case, the bond lengths in the seven-membered rings are very close to those of pure graphene (the previously mentioned strain of 1.7% being the largest among the seven bonds), and two of the bonds are actually initially shorter than those of pure graphene. Recomputation of the stress-strain curve corresponding to this grain boundary angle and pulling direction (shown in Fig. 2, right) indicates a strain at failure of 15.5% and an ultimate strength of 95 GPa, values that are approaching the strength of pure armchair graphene. Based on these results, we can conclude that grain boundaries with a mismatch angle of 28.7° do not affect the strength of armchair-oriented graphene sheets appreciably, whereas those with lower separation angles weaken them considerably.

The initial strain in the critical bonds for zigzag graphene pulled parallel to the boundary are 2.1%, 1.7%, and 0.7% for the 5.5°, 13.2°, and 21.7° grain boundary angles, respectively. The strains calculated through DFT are slightly higher at 3.2%, 2.2%, and 1.7%; however, the trend matches that of the MD simulations perfectly. Although the level of initial strain is lower for these critical bonds than those discussed for the perpendicular deformation direction, the general trend of decreasing strain with increasing grain boundary angle is the same and is consistent with the stress-strain results. For armchair graphene pulled parallel to the boundary, the critical bonds in the 15.8° and 21.4° are strained by factors of 5.4% and 4.0%, respectively, whereas those with lower separation angles weaken them considerably.

The initial stages of failure in (A to C) zigzag-oriented and (D to F) armchair-oriented graphene sheets pulled perpendicular to the grain boundaries.

We used MD and DFT calculations to study the mechanical strength of grain boundaries in zigzag- and armchair-oriented graphene sheets. For both orientations, we have found that the strain at failure and ultimate strength of graphene increases with grain boundary angle. We have looked in detail at the atomic-scale bond-breaking processes that lead to failure and have identified the critical bonds that determine the ultimate strength of the grain boundaries. Based on these analyses, it is clear that the initial strain in these bonds determines the failure strength: the higher the strain, the lower the strength. Higher grain boundary angles can better accommodate the seven-membered ring defects that make up the grain boundaries; therefore, the initial strain in the critical bonds decreases with increasing angle. Fracture mechanics methods were unable to predict the trends from our simulations because the influence of strained atomic bonds is inherently absent from continuum techniques.

Supporting Online Material
www.sciencemag.org/cgi/content/full/330/6006/946/DC1
Materials and Methods
Figs. S1 and S2
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References and Notes
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