Grain Boundary Effect on Electrical Transport Properties of Graphene

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ABSTRACT: The presence of grain boundary affects the mechanical strength, thermal dissipation, and charge transport of polycrystalline graphene flakes. There is still a debate on whether the electronic transmission is severely degraded by the grain boundary, especially between simulations and experiments. To address this issue, we performed electrical transport simulations based on π-orbital tight-binding Hamiltonian. Our results show that the intrinsic grain boundary is almost transparent for the carrier transport, but extrinsic chemical species (e.g., oxygen, hydroxyl) favor the adsorption on interdomain sites and increase the scattering substantially at the boundary region. The experiment, which shows degraded carrier transport due to grain boundary, can be plausibly explained with our theoretical results. To minimize the extrinsic effects of grain boundaries, we suggest doing electrical measurements under ultrahigh-vacuum condition after thermal annealing or applying pulsed current for desorbing the adsorbrates.

1. INTRODUCTION

Graphene, which is a monolayer graphite, has been considered to be one of the next generation materials in the semiconductor industry due to its appealing electronic, thermal, and mechanical properties. It was first produced by mechanical exfoliation from highly oriented pyrolytic graphite (HOPG) in 2004. However, HOPG possesses various kinds of extended defects such as monatomic steps, trenches, grain boundaries (GBs), etc. Identification of the structural details of these defects has been done via scanning tunneling microscopy (STM), where graphene has been used as a standard substrate in STM experiments for over 25 years. Due to the electronic coupling between the topmost layer and the graphite substrate underneath, the top layer graphene usually exhibits a triangular lattice with 0.246 nm periodicity. There has been also the observation of the honeycomb lattice, where different origins have been suggested such as multiple tip effect, lateral translation, and weakened coupling between the top two layers due to the lift-up of the surface layer by the STM tip. On the basis of the simultaneous observation of both triangular and honeycomb lattices, it was claimed that grain boundaries exist between two domains. The super periodicity of 1–10 nm, i.e., superlattices, has been evidenced in atomic-scale images, and the most probable reason is a rotation of the topmost layer on the graphite substrate. Such a superlattice extends hundreds of nanometers until interfacing with a neighboring domain of a different periodicity or orientation. The atomic structure of the grain boundary was first proposed in 2002. From this study, the boundary consists of pentagon and heptagon rings connected together. Such defects are expected to create localized electronic states, resulting in the bright strand in the STM image. Such localized states extending up to 4 nm away from a GB were observed in a recent experiment.

In order to facilitate graphene in the semiconductor industry based on carbon, synthesis of a large-size graphene flake is required. Atomically flat graphene sheets of micrometer scale in lateral size can be obtained on SiC surface by sublimating Si atoms. However, the electrical quality is dependent on the domain size after graphitization. For example, the C-terminated surface of SiC has a carrier mobility as high as 5000 cm²/(Vs), which is about 5 times that of the Si-terminated one. Accordingly, graphene grown on the C face has domain sizes more than 3 times larger than those grown on the Si face. Consistently, the carrier mobility was improved by 2 or 3 times when the terrace size of the Si face was enlarged by 5–8 times through graphitization under Ar gas annealing. Meanwhile, it is not likely that the step edges have a major negative impact on the carrier mobility, based on the measurement that the carrier mobility parallel or perpendicular to the edges is not significantly different. Hence, it has been claimed that the continuous graphene film is formed over the steps. Therefore, the number of domain boundaries other than terrace edges mainly affects the carrier mobility. Along with these indications of the presence of grain boundaries, it has been shown that two neighboring graphene regions with the same height and separated by a narrow intervening 6√3 domain have nonequivalent translations. This indicates that the GB is likely to be formed. Also the existence of the GB has been claimed in the STM, transmission electron microscopy (TEM),...
and optical microscopy measurements. In recent years, chemical vapor deposition (CVD) of hydrocarbon molecules on copper foils provides the community an economical way of producing large-area single-layer graphene with sparse distribution of multilayers. The predominant defect in these CVD graphene films is the grain boundary that is formed when neighboring nucleation sites expand and coalesce. A number of experimental efforts are devoted to decreasing the domain densities with fewer boundaries, which is expected to be an effective means to enhance the electrical transport property of CVD graphene. These efforts encompass a range of directions involving graphene production temperatures, methane/hydrogen partial pressures, copper foil surface crystallinity, and nucleation site density.

Grain boundary is therefore one of the main problems to be tackled to realize high-speed graphene-based devices. It is likely to degrade thermal and electron transport significantly. In experiments, contradictory results emerge about whether the presence of grain boundary degrades the charge transport across it. Yu et al. showed an increased resistance across grain boundary, whereas Huang et al. declared that grain boundaries are not particularly resistive. The recent experiment also shows that the interdomain connectivity of GB can affect electrical conductance. In theoretical works, studies on the electronic band structure and the stability in the presence of the grain boundary have been reported recently, which have shown that the Dirac point is not destroyed. Moreover, it is predicted that electron transport across GB would not be degraded that much. The discrepancy in experimental and theoretical works highlights the significance of understanding the impact of grain boundary on the interdomain electronic transport. Recently, several theoretical papers have investigated possible factors that might degrade charge transport across grain boundary. For example, the low transport mobility could be due to the GB dislocation density, the disorder of GB, and the average grain size and interdomain connectivity of GB. As GB is also a favorable site to adsorb extrinsic impurities (e.g., oxygen, hydroxyl, hydrogen, etc.) in experimental synthesis or measurement condition, in this work, we have investigated the GB effects on the electronic structure and how the adsorbed extrinsic impurities on GB sites affect the charge carrier transport of polycrystalline graphene.

2. THEORETICAL METHODS

2.1. Charge-Transport Model. The Hamiltonian of graphene, \( H \), is determined by the \( \pi \) orbital tight-binding method (\( \pi \)-TB), and the electron hopping parameter, \( t = -2.7 \) eV, is used to reproduce \( \pi \) band energy dispersion for graphene. The charge-transport property is calculated based on the nonequilibrium Green’s function (NEGF) method. The devices have source and drain electrodes, which are semi-infinite pristine graphene. The channel is in the mid region, where grain boundaries exist to scatter charge transport. In the NEGF method, the retarded Green’s function can be expressed as

\[
G = [E - H - \sum_i - \sum_D]^{-1}
\]

where \( \sum_i \) and \( \sum_D \) are self-energy terms to describe interactions between the channel and the source/drain electrodes, respectively. The energy-dependent electrical conductance can be defined as

\[
g = \frac{2e^2}{h} \text{Tr}(\Gamma_S \Gamma_D)
\]

where \( \Gamma_S(D) = i [\sum_S(D) - \sum_S(D)] \) are the energy-broadening matrices.

2.2. GB Model Structure. The GB model is a periodic arrangement of pentagon–heptagon pairs along the boundary proposed by ref 10. Two domains of an ideal honeycomb lattice along different orientations are combined together with a specific C–C bonding structure which comprises a GB. By adjusting lateral positions of carbon atoms at the GB, the pentagon–heptagon rings can be constructed along the boundary. In order to be energetically favorable, two domains have the same number of edge carbon atoms for a given length along the GB. Otherwise, incommensurateness will cause large strain energy, dangling bonds, or other defects. So, there is a specific misorientation angle between two domains at the favorable GB. To clarify this issue, we introduce chirality vector \( \mathbf{W}_c = ma_1 + na_2 = (m, n) \) as in CNT studies. Two graphene sheets are prepared with different \( \mathbf{W}_c \) vectors, and the edge is made to be parallel to the \( \mathbf{W}_c \) for each of them. When two domains are combined, the original \( \mathbf{W}_c \) vector has the meaning of periodic lattice vector along the GB, assuming the same length of the two \( \mathbf{W}_c \) vectors. In Figure 1, we illustrate an example of the shortest periodicity along GB. The \( \mathbf{W}_c \) indicated by \( (m, n) \) in Figure 1a has the length of \( \sqrt{7a} \) with \( a = 0.246 \) nm. There are 12 such vectors with the same length, represented by the arrows ending at the dotted circle. One can choose two different \( \mathbf{W}_c \) vectors arbitrarily, but 60° or its integer multiple angles difference should be avoided as it gives zero misorientation angle due to symmetry. For example, \((-2, 3)\) and \((-1, 3)\) are chosen in Figure 1. With combining two
of primitive lattice vectors of the rectangular cell \((T_1, T_2)\), which is along the \(y\)-axis. Along the \(x\)-axis, the shortest vector \(T_1 = 4a_1 + a_2\) and \(T_2 = -2a_1 + 3a_2\). \(T_2\) is one of the chirality vectors in Figure 1, and \(T_1\) is the shortest orthogonal vector with integer multiples of \(a_1\) and \(a_2\). (b) Its band structure by the \(\pi\)-TB method, and its density of states (DOS). (c) Periodic unit cell model with the GB. The periodicity requires two GBs of opposite tilt angles in the unit cell. The lattice vector \(a\) is the same as that in panel a. (d) Its band structure by the \(\pi\)-TB method and its density of states (DOS), shown in the right, are calculated by the \(\pi\)-TB method. Total DOS is shifted up for clarity, and local DOS are projected onto five or seven carbon atoms belonging to pentagon (‘penta LDOS’) or heptagon (‘hepta LDOS’) rings.

Figure 2. Comparison of electronic band structures with and without GB. (a) Rectangular supercell of ideal graphene with lattice vectors \(T_1 = 4a_1 + a_2\) and \(T_2 = -2a_1 + 3a_2\). \(T_2\) is one of the chirality vectors in Figure 1c. Within one periodic length along GB, there are one pentagon–heptagon pair and one hexagon. The angle of tilted orientation, \(\alpha\) in Figure 1, is 21.8°. As shown in ref 30, the GB is perfectly transparent or semiconducting depending on the chiralities of two domains. In this study, only transparent cases are considered to study the degrading effect of GB.

3. RESULTS AND DISCUSSION

3.1. Electronic Bands for Periodic Systems. The GB defects are expected to cause localized electronic states near the boundary. Assuming most part of the system is ideal graphene, we focus on how the GB affects the electronic band structure. First, we consider ideal graphene. For comparison with the GB results later, we choose a supercell with one lattice vector the same as one of the chirality vectors in Figure 1a. As shown in Figure 2a, our previous chirality vector \(-2a_1 + 3a_2\) is now one of theDirac point would be mapped into certain points along the \(\Gamma-X\) direction of the Brillouin zone. As shown in Figure 2b, the band structure calculated by the \(\pi\)-TB method shows that two Dirac points are mapped into \((0, 2\pi/3T_2)\) and \((0, 4\pi/3T_2)\). Since there are two ideal graphene domains in the system involving one GB, another chirality vector \(-a_1 + 3a_2\) needs to be checked. We confirmed that this also gives the same dispersion as shown in Figure 2b.

For the effect of GB, the periodic unit cells are constructed as shown in Figure 2c. The periodicity requires two GBs of opposite tilt angles in the unit cell. The GB is parallel to the \(y\)-axis. The lattice vector along \(y\)-axis \(T_2 = -2a_1 + 3a_2\) is the same as that of the previous ideal graphene case, while a different lattice vector \(U\) is used along the \(x\)-direction. Its band structure by the same \(\pi\)-TB method is shown in Figure 2d. Overall character of the energy gaps in Figure 2d is similar to that in Figure 2b, i.e., a significant energy gap (>2 eV) along \(\Gamma-X\) but metallic bands along the \(\Gamma-Y\) direction. Degenerate energy levels at \(\Gamma\) and \(Y\) points in Figure 2b are split in Figure 2d. But the Dirac point near the Fermi level remains almost the same, which is consistent with ref 31. This means the GB does not affect the electronic dispersion near the Dirac point. The total and local density of states (DOS) are computed, and the states localized at GB are shown in the right panel of Figure 2d. The shape of total DOS is significantly different from linear shape of ideal graphene, and it is strongly perturbed by GB induced localized states except near the Dirac point. The range of such defect states was measured to be 4 nm, so the strongly perturbed DOS in our result using \(|U| = 2\) nm can be understood. The first peak induced by GB defect appears 0.3 eV above or –0.4 eV below the Fermi level. This is well-consistent with STM experiment supporting the validity of the employed GB structure model.

3.2. Electron Transport across the GB. Electron transport across the GB is simulated with the model structure shown in Figure 3a. The periodic boundary condition is imposed along the transverse direction, and 64 \(k\)-points sampling along that direction are used to get smooth conductance curves. Figure 3b shows simulated conductance across the GB together with the ballistic conductance for ideal graphene. One can see that the conductance is quite close to the ballistic value (it is a factor of 0.76 at \(|E| < 1.5\) eV) although it shows larger decrease at \(|E| > 1.5\) eV. From Figure 3c, the local density of states at \(|E| < 1.5\) eV remains almost constant along the transport direction and increasing DOS can be seen with approaching the GB. This is also shown in Figure 3d. The increased DOS close to the GB is likely to enhance chemical reactivity with extrinsic defects. Although it decreases the ballistic conductance to a factor of 0.76, this is almost negligible compared to other environmental effects such as charged impurities and ripples which are ascribed to be main sources of mobility drawback. In addition, one can observe the bright stripe near the GB with the energy close to zero in Figure 3c, and this feature also can be seen in Figure 3d. This is reflecting localized states near the Fermi level as observed in the experiment.}

The experimentally accessible Fermi level for graphene is quite narrow in typically fabricated devices. The commonly used substrate is SiO₂ with a thickness of 300 nm. A relation between the graphene’s Fermi level \(E_F\) and the gate voltage \(V_g\) is given by \(V_g \approx 1000E_F^{0.58}\). Under the variation of \(V_g\) from 0 to 50 V, the \(E_F\) changes from 0 to 0.22 eV. In this range, we have seen the conductance is decreased less than 1 order by the
Therefore, the GB itself should not have significant impact on the measured conductance of graphene.

3.3. Extrinsic Effect on Conductance of GB. The carrier mobility of large-size graphene flakes, usually prepared by epitaxial methods, is on the order of 1000 cm²/(V·s),¹⁷,3⁸ which is 1 order lower than that of small flakes. It is said that polycrystalline character is mainly responsible for the mobility degradation in large flakes, assuming similar magnitudes of other environmental effects. The GB is one of the major defects existing in the polycrystalline structure, and our study shows that the intrinsic GB is not the limiting factor at all. Rather the main factor could be the extrinsic effect, which is passivation of the π-orbital at the GB. Since the GB is expected to be chemically reactive toward π-orbital passivation by foreign species, the conductance will be suppressed by π-orbital passivation. According to our ab initio density functional theory (DFT) calculations shown in Table 1, the chemisorption energies of O at the bridge site and H or OH at the top site of the GB are always larger than bulk site adsorptions. The ab initio calculation is done with VASP³⁹ based on the projector-augmented wave pseudopotential method. We have used local density approximation (LDA) and generalized gradient approximation (GGA) to describe the exchange-correlation functional terms. The effect of extrinsic π-orbital passivation at the GB has been studied in the following way. For a given GB passivation

Table 1. Chemisorption Energies of H, O, and OH Species at the Atomic Sites of Grain Boundary

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>bulk site</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>1.42 (1.11)</td>
<td>2.06 (1.66)</td>
<td>1.94 (1.56)</td>
<td>1.73 (1.49)</td>
<td>1.66 (1.31)</td>
<td>1.91 (1.55)</td>
<td>N/A</td>
<td>1.39 (1.00)</td>
</tr>
<tr>
<td>O</td>
<td>3.34 (2.50)</td>
<td>3.33 (2.49)</td>
<td>3.45 (2.61)</td>
<td>3.21 (2.16)</td>
<td>3.65 (2.79)</td>
<td>4.45 (3.52)</td>
<td>3.36 (2.54)</td>
<td>2.98 (2.09)</td>
</tr>
<tr>
<td>OH</td>
<td>2.00 (1.25)</td>
<td>2.48 (1.80)</td>
<td>2.24 (1.41)</td>
<td>2.09 (1.62)</td>
<td>2.14 (1.47)</td>
<td>2.31 (1.67)</td>
<td>N/A</td>
<td>1.64 (1.18)</td>
</tr>
</tbody>
</table>

*The adsorption sites are labeled in the figure below. The top sites are for H or OH, and the bridge sites are for O. Both ab initio results from LDA and GGA (in parentheses) are shown here.

*LDA and GGA predict σ-bonded C−O−C structure breaking the underlying C−C bond.
coverage, a corresponding number of $\pi$-orbitals belonging to pentagon or heptagon rings are removed according to the basic patterns shown in Figure 4a. With an increased coverage, more broken $\pi-\pi$ bonds occur at the GB sites. Thus, the number of $\pi-\pi$ connection pathways between the left and right regions of GB is narrowed, and the conductance is expected to decrease. Practically, the passivation sites for a given coverage concentration would distribute randomly. In this study, our focus is to understand the evolution of electrical conductance as extrinsic defects increase. With the basic patterns (e.g., A–D) shown in Figure 4a, a wide range of extrinsic defect coverage can be readily constructed to represent the diminished $\pi-\pi$ connection pathways as defect concentration increases.

The main conclusion of Figure 4b is that the conductance of the extrinsic GB can be largely reduced as compared with the intrinsic GB. This may explain that the electrical conductance measured within the graphene grain is several times higher than that for across GB.\(^2^9\) Also, large graphene flakes, like grown on SiC,\(^1^7\) exhibit 1 order lower carrier mobility than small mechanically exfoliated samples. Since the most electrical measurements are performed in ambient condition, this low carrier mobility is possibly due to the extrinsic effect rather than the intrinsic GB. Although high-symmetry GB is only considered in this study, the degradation of electrical property due to extrinsic defects should prevalently exist for GB with different intrinsic properties (e.g., symmetry, tilt angles, dislocation densities). Finally, it will be worthwhile to examine electrical behavior after removing extrinsic effects. According to the STM measurements in ultrahigh vacuum, the localized electronic states, caused by intrinsic GB, are visible after heating HOPG at 500 °C.\(^1^1\) With the similar treatment method, the carrier mobility of graphene with GB could be further enhanced.

4. CONCLUSION

In summary, our theoretical investigation shows that the intrinsic GB is almost transparent to the carrier transport. However, foreign species are shown to favor the adsorption on the boundary sites, resulting in the passivation of the available $\pi$-orbital with a degraded electronic transport. Probably, the experimentally observed degradation of the charge transport across the grain boundary in graphene is not caused by the intrinsic grain boundary but the passivated grain boundary by extrinsic contaminants. We suggest experimentalists eliminate the extrinsic effects at GB sites by thermal annealing or pulsed current, with the subsequent electrical measurements of the CVD graphene under ultrahigh-vacuum condition.

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\textbf{Notes}

The authors declare no competing financial interest.

\section*{ACKNOWLEDGMENTS}

This work is supported by Nano-Material Technology Development Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT and Future Planning (2012M3A7B4049888).

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