Grain Boundary Resistivity in Polycrystalline Graphene

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Abstract

In recent years, graphene has emerged as a favorable material for a wide range of technological applications [1]. In particular, its high room-temperature mobility, unique dispersion relation, and advantageous mechanical properties make graphene an exciting substance for the realization of next-generation electronic devices [2,3]. While single-crystal graphene would be an ideal choice, the most promising approach for the mass production of large-area graphene is chemical vapor deposition (CVD), which usually results in a material that is polycrystalline [4,5]. This polycrystallinity arises due to the nucleation of growth sites at random positions and orientations during the CVD process. In order to accommodate the lattice mismatch between misoriented grains, the grain boundaries in polycrystalline graphene are made up of a variety of non-hexagonal carbon rings, which can serve as a source of scattering during charge transport [6,7]. Indeed, several experimental works have demonstrated that grain boundaries add an extra resistance compared to single-grain samples [8-10]. Thus, in order to understand the large-scale transport properties of polycrystalline graphene, it is important to understand the scattering mechanisms associated with the grain boundaries.

In this work, we use numerical simulations to examine the role that grain boundaries play in charge transport through polycrystalline graphene. We find that the presence of grain boundaries increases the sheet resistance of graphene samples, and by employing a simple scaling law we can extract the intrinsic grain boundary resistivity from our simulations. A comparison to experiment reveals that the calculated grain boundary resistivity is 1-2 orders of magnitude smaller than what is obtained from experimental measurements. This suggests that scattering due to the non-hexagonal structure of the grain boundaries is relatively small, and that another mechanism must be responsible for most of the experimentally-measured grain boundary resistivity.

To calculate the sheet resistance of polycrystalline graphene, we use a real-space order-N quantum wave packet approach to compute the Kubo-Greenwood conductivity [7]. In this approach, the zero-frequency conductivity for charge carriers is given by

$$\sigma_{DC}(E) = \frac{e^2}{4}\rho(E)\lim_{t\to\infty}\frac{\partial}{\partial t}\Delta X^2(E,t), \quad (1)$$

where $\rho(E)$ is the density of states and $\Delta X^2(E,t)$ is the mean-square spreading of the wave packet. From this, we can calculate the sheet resistance of a polycrystalline graphene sample as $R_S = 1/\sigma_{DC}$. By doing this calculation for samples of varying grain size, we can extract the grain boundary resistivity according to a simple scaling law,

$$R_S = R_S^0 + \frac{\rho_{GB}}{l_G}, \quad (2)$$

where R_S^0 is the sheet resistance of an individual grain, ρ_{GB} is the grain boundary resistivity, and l_G is the average diameter of each grain.

The results of these simulations can be seen in Fig. 1, where we plot the sheet resistance of polycrystalline graphene as a function of the average grain size. The blue squares are from our simulations, and the blue dotted line is a fit to this data using Eq. (2) and assuming that $R_S^0 = 0$. From this fit we extract a grain boundary resistivity of $\rho_{GB}^{sim} = 0.064\,\text{k}\Omega\text{-}\mu\text{m}$. For comparison, we also plot the sheet resistance of polycrystalline graphene measured by Duong et al [8]. The red circles indicate their measurements, and the red dotted line is the fit to Eq. (2). From this fit, we extract $R_S^0 = 130\,\Omega$ and

$\rho_{GB}^{exp} = 1.4\,k\Omega\text{-}\mu m$, which is 20x larger than the theoretical value. Table 1 shows a summary of the values of ρ_{GB} extracted from a variety of experimental measurements. In all cases, the experimental value is 1-2 orders of magnitude larger than our calculated value.

These results suggest that the scattering due to the non-hexagonal structure of the grain boundaries is relatively small, and that another mechanism must be responsible for most of the experimentally-measured grain boundary resistivity. It has been shown experimentally that the grain boundaries tend to be highly reactive compared to pristine graphene [4,8,11,12], resulting in a great deal of functionalization between individual grains. Therefore, our future work involves a study of the effect that grain boundary functionalization has on the charge transport properties of polycrystalline graphene.

References

[1] A. K. Geim, *Science* **324** (2009), 1530-1534.
[2] K. S. Novoselov, *Rev. Mod. Phys.* **83** (2011), 837-849.
[3] A. H. Castro Neto et al., *Rev. Mod. Phys.* **81** (2009), 109-162.
[4] P. Y. Huang et al., *Nature* **469** (2011), 389-392.
[5] K. Kim et al., *ACS Nano* **5** (2011), 2142-2146.
[6] O. V. Yazyev and S. G. Louie, *Nat. Mater.* **9** (2010), 806-809.
[7] D. van Tuan et al., *Nano Lett.* **13** (2013), 1730-1735.
[8] D. L. Duong et al., *Nature* **11** (2012), 235-240.
[9] Q. Yu et al., *Nat. Mater.* **10** (2011), 443-449.
[10] A. W. Tsen et al., *Science* **336** (2012), 1143-1146.
[11] P. Nemes-Incze et al., *Appl. Phys. Lett.* **99** (2011), 023104.
[12] A. Salehi-Khojin et al., *Adv. Mater.* **24** (2012), 53-57.

Figures and Tables

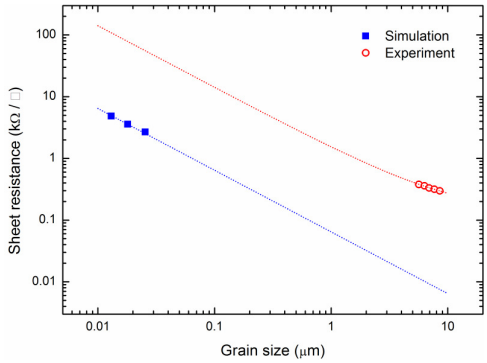

Fig. 1. Sheet resistance of polycrystalline graphene as a function of average grain size. The blue squares are the results of numerical simulations and the red circles are measurements from Ref. [8]. The dotted lines are fits using the scaling law in Eq. (2).

Source	Grain size	$\rho_{GB}(k\Omega\text{-}\mu m)$	$\rho_{GB}^{exp}/\rho_{GB}^{sim}$
This work	13 – 25 nm	0.064	1
Duong et al. [8]	5 – 9 μm	1.4	22
Yu et al. [9]	5 – 10 μm	8	125
Tsen et al. [10]	1 μm	0.5 – 4	8 – 63

Table 1. Comparison of theoretical and experimental grain boundary resistivity. The first row shows our numerical results, and the subsequent rows show the experimental results.