Two-dimensional sheet resistance model for polycrystalline graphene with overlapped grain boundaries

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ABSTRACT

Overlapped grain boundaries (OGBs) are an important feature of two-dimensional (2D) materials that are electrically, mechanically, and thermally different from conventional grain boundaries (CGBs). The properties of an individual OGB have been explored in some microscopic studies, but the effects of OGBs on the macroscopic properties of 2D materials such as sheet resistance and mobility have rarely been investigated. Therefore, it is necessary to identify and formulate the influence of the OGBs on the macroscopic properties of 2D materials.

In this study, we propose a 2D sheet resistance and mobility model for polycrystalline graphene that considers the effects of OGBs and intra-grain defects. The proposed model is supported by a simulation of the growth and sheet resistance of graphene grown by chemical vapor deposition (CVD). The electrical properties were investigated with respect to the average grain size, and a threshold grain size for mobility saturation was introduced, which can provide directions for the growth of high-quality 2D materials for commercial use. Moreover, the 2D characteristics reflected in the model can explain the variation in the sheet resistance and mobility of graphene grown under the same conditions. Since this model is applicable to general 2D materials, it will provide guidelines for the growth of various 2D materials.

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Introduction

A conventional grain boundary (CGB) is known as a one-dimensional (1D) line defect that is formed between adjacent grains of chemical vapor deposition (CVD)-grown two-dimensional (2D) materials [1–4]. According to microscopic studies, the resistivity of an individual CGB is much higher than the intra-grain resistivity [2,3]; thus, it is the main cause of the degradation of electrical properties in polycrystalline materials. Macroscopically, this effect can be formulated as a function of the average grain size in thin film materials [5–7] because the proportion of CGBs is inversely proportional to the average grain size. In this case, the electrical properties improve as the average grain size increases.

Similarly, with an increase in the average grain size being needed in order to improve the electrical properties of graphene [8,9], corresponding sheet resistance models for polycrystalline graphene that depend on the average grain size have been proposed [10–13]. These studies explained the tendency of the sheet resistance to decrease with increasing average grain size, but they could not explain the variations in both the sheet resistance and mobility in graphene grown under the same conditions [11,14–16]. Moreover, these models were not very accurate because they were 1D-approximated or experimentally fitted models.

In addition, the previous sheet resistance models did not take into account the overlapped grain boundaries (OGBs), which are prevalently formed during the CVD growth of 2D materials such as graphene and MoS_2 [4,17,18]. OGBs, in the form of local bi-layers in the overlapped regions (Fig. S1B), improve the local electrical properties of graphene, whereas conventional grain boundaries (CGBs), which are atomically stitched boundaries (Fig. S1A), are the main cause of electrical degradation. Therefore, it is very important to identify and formulate the effects of OGBs, and to incorporate these effects into sheet resistance models.

In the present study, the growth and sheet resistance of CVD-grown graphene are simulated considering the effect of OGBs by the Monte Carlo method. We propose a macroscopic 2D sheet resistance and mobility model as a function of average grain size and investigate the effect of OGBs and intra-grain defects on the graphene. In this case, we introduce a threshold grain size at which mobility is saturated, which is an important parameter for the growth of 2D materials. Moreover, we find that the sheet resistance and mobility vary with the grain size distribution and the grain arrangement, which are 2D characteristics. Since the proposed model can be generally applied to 2D materials such as transition metal dichalcogenides (TMDCs) and hexagonal boron nitride (h-BN) as well as graphene, it will also provide general guidelines for the growth of 2D materials.

Methods

Custom-made simulation tools were used to explore the influence of OGBs on electrical properties. In detail, the method is divided into two steps: generating a graphene sheet with various grain size distributions and calculating the sheet resistance of the structure. For the first step, seed points for the initiation sites of nucleation were randomly generated within a given simulation area (100–2025 μm^2) assuming periodic boundary conditions (PBC). The number of seeds was determined according to the average grain size and corresponding number density. The simulation area was divided by meshes, wherein the size of each mesh was 500 nm × 500 nm. The meshes were grouped according to the index of the nearest seed point, assuming the growth rate of each grain was the same, to generate randomly arranged grains as shown in Fig. S2C. Each mesh was assumed to be connected to nearby meshes by a resistor, whose resistance corresponded to the intra-grain sheet resistance (R_0) of 150 Ω/sq between meshes in the same group and corresponded to the 2D CGB resistivity (ρ_{CGB}) of 1 kΩ μm between meshes in different groups. These resistivity values were determined theoretically and experimentally [12,13,19]. The sheet resistance was calculated from the circuit, and it agreed well with the existing 1D sheet resistance equation [12,13] (see Figs. S2A and B).

Results and discussions

Sheet resistance model with overlapped grain boundaries

The simulated grain size distribution of graphene with an average grain size of 5 μm is represented in Fig. 1B. Here, the obtained distribution agreed well with the observed distributions resulting from the time-dependent nucleation processes [20,21], and followed a Gaussian distribution. From the obtained distribution, the standard deviation (σ) and average (L_G) of the grain size were calculated for each simulation. When the simulation steps were repeated 500 times, a distribution of σ/L_G was obtained, as shown in Fig. 1C. The expected value of σ/L_G was 0.25, and it was often between 0.2 and 0.32, which was similar to the experimental values of σ/L_G [20,21]. However, these values could differ because the grain size was not strictly defined in previous experimental articles. In this study, the grain size was defined as the square root of the grain area.

A very recent study on the formation mechanism of OGBs implied that on average, about 40% of all GBs could be overlapped with random misorientation angles under certain growth conditions [22]. In this case, an individual OGB was found to improve the electrical properties by forming a local bilayer [18,23], and the resistivity of the OGB (ρ_{OGB}) was lower than the intra-grain resistivity (ρ_G). Based on these results, we derived a 1D sheet resis-

tance equation that considered the influence of OGBs, as shown in the Supplementary Information (Eq. S2).

Since the 1D approximation model considered only the average grain size as a variable, it could not reflect the grain size distribution. However, the grain size distribution affected the sheet resistance even when the average grain size was held constant. To consider the grain size distribution when calculating the sheet resistance, σ/L_G is an important parameter that helps to determine the specific shape of grain size distribution, which was assumed to be Gaussian. The sheet resistance equation considering this effect is derived in the Supplementary Information (Eq. S3) and it is represented by

$$R_{sh} = R_0\left(1 + \frac{\gamma\lambda(1 - P_{OGB})}{L_G}\right). \tag{1}$$

γ is the factor caused by the grain size distribution and it is calculated to be 0.94 for σ/L_G = 0.25 (Table S1). P_{OGB} is the proportion of OGBs among all GBs. R_0 is the sheet resistance as L_G approaches to infinity, i.e., the intra-grain sheet resistance. λ is defined as ρ_{CGB}/R_0. In this case, R_0 was set to 150 Ω/sq, which is the extrinsic limit on SiO$_2$ [19], and ρ_{CGB} was set to 1 k$\Omega\cdot\mu m$ [12,13].

Next, there were many ways of arranging the grains, and each arrangement exhibited a different sheet resistance (Fig. S2C). This effect occurred even if σ and L_G were the constant and the grain size distributions were the same. In Figs. S2B and C, the x-direction represents the channel length and the y-direction represents the channel width. In this case, n_{CGB} is defined as the number of CGBs that current passes through when flowing along the direction of the channel length (x-direction in Fig. S2C). Note that n_{CGB} is constant regardless of the y-coordinate in the 1D model (Fig. S2B). In contrast, n_{CGB} is not constant and depend on the y-coordinate in the 2D model (Fig. S2C). This non-uniformity of n_{CGB} reduces the sheet resistance in the 2D model because it can be considered as parallel connections of resistors, which are calculated by the harmonic sum. We defined α as the coefficient of this effect, and the sheet resistance equation is thus described by

$$R_{sh} = R_0\left(1 + \frac{0.94\alpha\lambda(1 - P_{OGB})}{L_G}\right). \tag{2}$$

As the channel length becomes shorter, α becomes smaller. If the channel length is sufficiently long, α approaches 1 as the non-uniformity of n_{CGB} disappears. In this case, α was constant at 1 in the 1D sheet resistance model because n_{CGB} was uniform. Therefore, the 2D sheet resistance was lower than the 1D sheet resistance due to the above two factors of α and γ (Fig. S2A). In this study, we fixed the average of n_{CGB} to 5 for consistency, and the corresponding value of α was 0.815, as shown in Fig. S5B.

Fig. 1D shows the effect of the OGBs on sheet resistance. The simulation was repeated 500 times per point on the graph, and the standard error was less than 1%, as shown in Fig. S3. The proposed equation and the simulation data were in good agreement that the sheet resistance decreased as P_{OGB} increased.

In this case, the role of OGBs in the sheet resistance was that of a bridge between two adjacent grains, and the effective grain size was increased by the OGBs. Fig. S4A shows the sheet resistance for graphene when P_{OGB} = 0.2 (blue line), the sheet resistance for replacing OGBs with mono-layer graphene (black line), and the sheet resistance for replacing OGBs with bi-layer graphene (red line). In these cases, the sheet resistance was almost same. In addition, the sheet resistance was hardly affected by the overlap length of the OGB (Fig. S4B). This was because the intra-grain resistivity and OGB resistivity were of a similar order of magnitude, whereas the CGB resistivity was extremely high. The area proportion of GBs was so low that a resistivity difference of several times did not affect the total sheet resistance of graphene. This meant that an