Effect of additional annealing on the electrophysical properties of large-size CVD-graphene samples

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Abstract. This paper is devoted to the comparative study of the resistivity temperature dependences for large-size 1–2 layered graphene samples prepared by the CVD method and subjected to additional annealing in an Ar/H mixture at different temperatures. The influence of the annealing temperature on the temperature dependences of resistivity was qualitatively analyzed for two types of initial samples demonstrating a metallic- or semiconductor-like \( \rho(T) \) dependence. This made it possible to elucidate the processes occurring in the samples upon annealing, as well as to assess the degree of their influence on the electrical properties of the annealed samples. This analysis showed that the main processes initiated by annealing are the formation of additional defects and cleaning of the graphene surface. To confirm this conclusion, we performed a numerical analysis of the experimental \( \rho(T) \) dependences, based on a model taking into account different scattering mechanisms of charge carriers in graphene samples. This allowed us to determine the concentrations of impurities on the graphene surface and defects in the graphene crystal structure for all investigated samples. The character of the change in these values depending on the annealing temperature for samples with different types of the \( \rho(T) \) dependence is discussed.

1. Introduction

Graphene is a two-dimensional allotropic modification of carbon, which, along with fullerenes, nanodiamonds and carbon nanotubes, has attracted increased interest from researchers. Due to its unique properties, graphene has already found application in various fields of electronics and the scope of its possible practical use is constantly expanding [1]. The specific energy structure of graphene, which contains a zero energy gap, leads to a lot of unusual physical properties of this material, such as the anomalous quantum Hall effect, the field effect, and the Klein paradox [2]. The most appropriate method for the synthesis of large-size graphene samples is chemical vapor deposition (CVD) on metal foils followed by a transfer to different substrates [3]. However, due to the technological features of this method, the properties of the obtained graphene samples significantly depend on the synthesis and transfer parameters, including uncontrolled ones. On the other hand, the two-dimensional structure of graphene makes it quite easy to change its properties (including the transport ones) by various external influences. This is why different post-processing methods are used to modify the properties of synthesized graphene samples. Among them are the intercalation of different atoms into graphene layers [4], the impurity deposition on the graphene surface [5], ion bombardment of synthesized samples [6],
and their additional annealing in a mixture of gases [7]. In this work, we investigate the effect of additional annealing at different temperatures on the temperature dependences of the resistivity in large-size CVD-graphene samples.

2. Samples and experimental details
Our samples were synthesized by the CVD method from a gas mixture of methane, hydrogen, and argon on copper foil substrates of 25 μm in thickness. These substrates were preliminary annealed in an Ar/H₂ mixture for 1 h. The synthesis was performed at a temperature of 1000°C for 15 min. By this process, we have obtained 1–2 layered graphene samples. This was confirmed by determining the ratio of G and 2D peaks in the Raman spectra, which are often used to estimate the number of graphene layers according to the result of [8]. Then, the synthesized graphene coatings were transferred onto Si/SiO₂ substrates by using PMMA. Additional annealing of the graphene samples was performed under ambient pressure in a mixture of argon and hydrogen (in a ratio of 9 to 1) at different temperatures (250°C and 400°C) for 30 min. To perform the resistive measurements, we used samples of large size (about 1x1 cm²). The temperature dependences of the resistivity in the temperature range from 77 K to 300 K were measured by the standard ac four-probe method using the van der Pauw geometry. Contacts to graphene samples were made with a conductive silver paste. The measurements were performed twice with changing current and voltage contacts. The resistivity was calculated using the van der Pauw formula and taking into account the value of a correction factor depending on the ratio of two measured resistivity values.

3. Experimental results and discussion
According to the results of resistive measurements, the synthesized graphene samples can demonstrate the ρ(T) dependence of two different types: metallic-like (the resistivity value decreases with decreasing temperature in the entire measurement range) or semiconductor-like (the resistivity value starts to increase with decreasing temperature in the low-temperature range). Such a difference is obviously resulted from uncontrolled processes occurring during the synthesis of samples and their transfer to Si/SiO₂ substrates. One can assume that, as a result of such processes, the obtained samples differ in the number of defects and/or adsorbed contaminants on their surface, as well as in the block structure of graphene layers, which leads to a change in the dominant mechanism of charge-carrier scattering. According to [9], in graphene samples with a metallic-like ρ(T) dependence, scattering of acoustic phonons plays the role of the main scattering mechanism, while in samples with a semiconductor-like ρ(T) dependence, impurity scattering is dominant.

Figure 1 shows the modification of the temperature dependences of the resistivity upon additional annealing at temperatures of T = 250°C and T = 400°C for two samples demonstrating a metallic-like ρ(T). One can see that after annealing at T = 250°C, the resistivity value decreases, which indicates an improvement of the sample quality. It is reasonable to assume that annealing results in the cleaning of the sample from different uncontrolled contaminants (absorbed on its surface during the processes of sample synthesis and transfer from a copper foil to a Si/SiO₂ substrate) and/or from defects located on the substrate surface, which influences the process of charge transfer in the graphene layers. After annealing at T = 400°C, the absolute value of the resistivity increases. This indicates that even if the process of surface cleaning becomes more intense, new defects in the graphene structure appear simultaneously due to the bombardment with high-energy argon atoms, the latter having a stronger impact on the resistivity value.

The temperature dependences of the resistivity for the sample initially demonstrating a semiconductor-like ρ(T) dependence, obtained after additional annealing of this sample at T = 250°C and T = 400°C, are shown in figure 2. It is seen that, contrary to the previous case, additional annealing has a slight effect on the resistivity value at room temperature but results in a significant weakening of the resistivity growth at low temperatures. This shows that for samples with a semiconductor-like resistivity behavior, despite the expected increase in the number of defects with increasing annealing temperature, the effect of surface cleaning remains dominant with respect to the change in the resulting
quality of the sample. This may be related to the higher amount of adsorbed contaminants on the surface of the initial sample, which was the reason for the observed semiconductor-like $\rho(T)$ dependence.

**Figure 1.** Influence of annealing at different temperatures on the resistivity in samples with the initial metallic-like $\rho(T)$ dependence. Symbols are the experimental data; lines present the results of our calculations.

**Figure 2.** Influence of annealing at different temperatures on the resistivity in samples with the initial semiconductor-like $\rho(T)$ dependence. Symbols are the experimental data; lines present the results of our calculations.

Thus, the effect of additional annealing on the graphene resistivity depends on the type of its temperature dependence for the initial sample. For samples with the initial metallic-like $\rho(T)$ dependence, the effect of graphene surface cleaning from adsorbed contaminants is dominant for low-temperature annealing ($T = 250^\circ C$) and results in an improvement of the sample quality. With increasing
annealing temperature, the effect of the formation of additional defects in the graphene structure begins to play an increasingly important role, and the sample quality deteriorates. For samples with the initial semiconductor-like $\rho(T)$ dependence, the effect of graphene surface cleaning remains predominant with an increase in the annealing temperature up to $T = 400^\circ C$, thus, such annealing continues to improve the sample quality.

To quantitatively confirm our conclusions, below we use the model proposed in [9] to describe the $\rho(T)$ dependences in graphene samples with taking into account different mechanisms of charge carrier scattering. To obtain more reliable results, we have additionally analyzed the resistivity data taken from [10]. The graphene samples discussed in [10] were synthesized using the same setup, and the processes of synthesis, transfer, and additional annealing completely coincide with the ones we used. This allows us to analyze the $\rho(T)$ dependences taken from [10] together with our data. The experimental data we used are shown in figure 3. Note that for the case of the initial semiconductor-like $\rho(T)$ dependence, the additional sample annealing was performed in [10] at a significantly higher temperature ($T = 750^\circ C$), which gives us additional information for analyzing the effect of annealing on the graphene properties.

![Figure 3](image-url)

**Figure 3.** Resistivity for CVD-graphene samples taken from [10]. Symbols are the experimental data; lines present the results of our calculations.

The theoretical model developed in [9] makes it possible, based on the semi-classical Boltzmann transport theory, to derive equations for the relaxation time in cases of different scattering mechanisms. Using these equations, it is possible to calculate the contributions to resistivity from considered scattering types, as well as the total resistivity value at different temperatures. The concentrations of charge impurities located on the graphene surface, $n_i$, and defects in its crystal structure, $n_D$, were estimated by fitting the results of calculations considering scattering by Coulomb impurities, acoustic phonons, and neutral defects with the experimental data for all studied samples. The results of our calculations of the $\rho(T)$ dependences are shown by solid lines in figures 1, 2, and 3 together with the experimental data. One can see that the fitting results are reasonable, which allows us to determine the $n_i$ and $n_D$ values quite unambiguously. The results of our calculations are presented in table 1 and will be briefly analyzed below to validate our previous assumptions about the reasons for the change in graphene properties upon additional annealing.
Table 1. Parameters of the studied samples, calculated using the model [9]

| Sample                     | $n_i$ $(10^9 \text{ cm}^{-2})$ | $n_D$ $(10^9 \text{ cm}^{-2})$ |
|----------------------------|-------------------------------|-------------------------------|
| S1 as-prepared             | 2                             | 1.48                          |
| S1, $T = 250^\circ \text{C}$ | 1.2                           | 1.44                          |
| S2 as-prepared             | $< 0.01$                      | 1.30                          |
| S2, $T = 400^\circ \text{C}$ | $< 0.01$                      | 1.48                          |
| SL2 as-prepared [10]       | $< 0.01$                      | 1.35                          |
| SL2, $T = 250^\circ \text{C}$ [10] | $< 0.01$                      | 1.14                          |
| S3, $T = 250^\circ \text{C}$ | 3.6                           | 1.18                          |
| S3, $T = 400^\circ \text{C}$ | 1.3                           | 1.58                          |
| SL1 as-prepared [10]       | 3.1                           | 1.0                           |
| SL1, $T = 750^\circ \text{C}$ [10] | 0.8                          | 1.1                           |

Let us first consider the results obtained for samples with a metallic-like $\rho(T)$ dependence. As expected, for most of them the concentration of impurities is very low (see table 1), therefore the resistivity behaviour in these samples is mainly affected by the defect concentration. Despite the fact that we used different samples for our analysis, the results obtained suggest that there is a clear trend in the variation of the defect concentration with annealing temperature. As seen in figure 4(a), low-temperature annealing (at $T = 250^\circ \text{C}$) reduces the number of defects existed in the initial samples, but a further increase in the annealing temperature results in an increase in the $n_D$ value, which indicates the activation of the formation of new defects. Thus, the quality of such samples can be slightly improved by using only low-temperature annealing.

![Figure 4a](image1.png)

**Figure 4a.** Variations of the calculated concentration of defects in graphene samples with a metallic-like $\rho(T)$ dependence (a) and the surface impurity concentration in samples with a semiconductor-like $\rho(T)$ dependence (b) depending on the temperature of additional annealing.

For both samples with a semiconductor-like $\rho(T)$ dependence (our sample S3 and sample SL1 from [10]), there is a tendency to a decrease in the defect concentration with increasing annealing temperature (see table 1). However, for these samples, the resistivity behaviour is mainly affected by the variation in the impurity concentration upon annealing, since it is the presence of impurities that leads to an increase in the resistivity with decreasing temperature. The variation of the $n$ value with annealing temperature is shown in figure 4(b). The concentration of impurities is seen to decrease consistently with increasing annealing temperature up to $T = 750^\circ \text{C}$. As a result, contrary to samples with a metallic-
like $\rho(T)$ dependence, the quality of samples with the initial semiconductor-like one continues to improve when using additional annealing at higher temperatures. Thus, for such samples, sample surface cleaning during annealing is the process that determines their resulting quality even at high annealing temperatures. In addition, one can speculate that annealing at high temperatures additionally affects the block structure of graphene layers (analogously to the case of thin copper films [11]), which can also result in a weakening of the activation character of the $\rho(T)$ dependence at low temperatures.

Thus, the numerical analysis of the experimental $\rho(T)$ dependences, based on the model [9] confirms our above assumptions about the processes occurring in CVD-graphene samples during their additional annealing. Our hypothesis on the relative degree of influence of these processes on the conductive properties of the initial samples, depending on the $\rho(T)$ dependence type and the temperature of additional annealing was also confirmed.

4. Conclusions
In this paper, we have experimentally investigated the modification of the resistivity temperature dependences for large-size CVD-graphene samples upon their annealing in an Ar/H mixture at different temperatures. By numerical analysis of these dependences, we have determined the concentrations of defects in the graphene structure and impurities on the sample surface, and analyzed the influence of different processes occurring upon annealing on the conductive properties of samples with initially different types of the $\rho(T)$ dependence. It is concluded that additional annealing of the samples is accompanied by two main processes: graphene surface cleaning from adsorbed contaminants and the formation of additional defects in the graphene structure. Which of these processes dominantly affects the conductive properties of the annealed sample is determined by the quality of the initial sample and the annealing temperature. For samples demonstrating a metallic-like $\rho(T)$ dependence, only low-temperature annealing improves their quality due to a decrease in the number of existing defects, since an increase in the annealing temperature up to $T = 400^\circ$C initiates the formation of new defects in the graphene structure. The conductive properties of samples with the initial semiconductor-like $\rho(T)$ dependence are mainly determined by the concentration of impurities on their surface. In this case, an increase in the annealing temperature up to $T = 750^\circ$C leads to a consistent decrease in the concentration of these impurities, so that the sample quality continues to improve.

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