Variation of the resistivity and chemical composition of CVD graphene under annealing in a reductive atmosphere

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Abstract. Graphene samples synthesized by chemical vapor deposition, transferred onto Si/SiO₂ substrates by the standard technology using PMMA, and then annealed in a reductive atmosphere have been characterized by XPS observations and measurements of the resistance temperature dependence. It was shown, that most of as-transferred samples exhibit a metallic-like resistivity dependence but some of them can demonstrate a non-metallic one. A comparative analysis of the results obtained by the XPS study and resistance measurements allowed us to conclude that the conduction process in CVD graphene is directly affected by functional groups adsorbed on the sample surface. Annealing in a mixture of H₂ and Ar at T = 250–750°C is shown to result in a cleaning of the graphene surface from adsorbed contaminations and in a modification of the resistance temperature dependence which demonstrates a higher slope in case of a metallic-like behavior for as-transferred samples and a suppression of the activation-type dependence in case of a non-metallic one.

1. Introduction

Modern two-dimensional (2D) single layer structures, such as graphene, phosphine, dichalcogenides of transition metals attract growing interest due to their electronic, optical, mechanical, and other properties promising various applications. Graphene has recently become one of the most popular 2D materials for nano- and optoelectronic applications [1, 2]. Graphene is characterized by very high mobility of charge carriers at room temperature and a manifestation of a number of quantum effects (the Hall effect, the ballistic transport effect, etc.) at low temperatures, as well as by high transparency, electrical and thermal conductivity [3]. This makes it an ideal candidate for using in future electronics and energy harvesting devices, such as conducting electrodes, switches, sensors, etc. However, impurities and topological defects arising during the graphene synthesis and/or transfer process can substantially affect its electronic properties and the performance in these devices, so the quality of graphene layers is crucial for these applications [2].

Chemical vapor deposition (CVD) of graphene utilizing copper as a catalyst is one of the most promising methods for producing continuous layers of a high quality graphene over a large area [4]. CVD synthesis is determined by a large number of technological parameters, and since some of them are difficult to control, the samples synthesized at the same specific parameters may differ essentially from each other. The transfer of the graphene layer onto a nonconductive substrate is a multistep procedure, which is fraught with introducing chemical and morphological defects. For this reason, controlling the graphene quality during the synthesis and transfer procedure is a difficult task, especially when working in ambient conditions. X-ray photoelectron spectroscopy (XPS) is one of the basic analytical methods used for the characterization of carbon-based materials, especially graphene-
related ones. The XPS study allows to identify the sp$^2$-hybridized carbon which characterizes C–C bonds in graphene layers itself, the sp$^3$-hybridized diamond-like carbon in defect sites of graphene, carbides, vacancy-type defects, and a carbon bound to oxygen in various functional groups [5–7]. Except for the above, the integral intensity of the core level C1s peak gives an information on an average thickness of a continuous carbon layer [8].

Another way to control the graphene sample quality is the measurements of the resistivity, $\rho$, temperature dependence. Usually, CVD graphene is characterized by a granular structure so that the grain boundaries give a contribution to the measured resistivity value. As a result, in most cases the resistivity demonstrates a non-metallic behavior (i.e., its value increases with decreasing temperature), especially in case of a few-layer graphene [9]. A metallic-like $\rho(T)$ dependence for both few-layer [10] and monolayer [11] graphene samples can be obtained when measuring with a distance between electrodes of several microns thus excluding the grain boundary influence.

It is reasonable to assume that an annealing in a reductive atmosphere can result in a removal of a polymer residue and functional groups adsorbed from the ambient atmosphere on the graphene surface, leading to the subsequent changes in the electronic and structural properties of samples. For this reason, the aim of this work is to trace the correlation of the chemical composition evolution of transferred CVD graphene under annealing and its electrical properties on a macroscopic scale.

2. Methods
Graphene samples were synthesized using the CVD technique from a gas mixture of methane, hydrogen, and argon to copper foil substrates (Alfa Aesar; thickness is 25 microns). Before synthesis, the polished copper substrates were annealed in a mixture of argon and hydrogen for 1 h. Synthesis was carried out for 15 min at a temperature of 1000°C. The process was conducted at a reduced pressure; the flow rates of hydrogen, methane, and argon were 5 ml/min, 50 ml/min, and 250 ml/min, respectively. The synthesized graphene layers were transferred onto a nonconductive substrate by the standard technology, i.e., the graphene film on one side of the Cu foil was coated with poly(methyl methacrylate) (PMMA) and placed in an aqueous solution of iron chloride to dissolve Cu on the unprotected side. The PMMA film that carries the graphene layer was rinsed several times with distilled water to minimize the chemical contamination, and then transferred onto a silicon substrate covered with thermally grown SiO$_2$ of 285 nm thickness. After the transfer, the sample was allowed to dry, and the PMMA was dissolved in acetone at a temperature of 200°C. After characterization, the samples were additionally annealed at temperatures of 250–750°C in a mixture of H$_2$ and Ar at a ratio of 1:9 for 30 min.

XPS analysis was performed on a Thermoscientific K-alpha using Al Ka radiation (1486.6 eV). Measurements of the samples on nonconductive substrates were made using an electric flood gun for charge compensation. The spectra were collected in vacuum ($10^{-5}$ mbar) with a spot diameter of 400 µm. The peaks were fitted with Voigt functions having the 70 % Gaussian and 30 % Lorentzian character, after a Shirley background subtraction. The peak of sp$^2$ of C–C bond was fitted using an asymmetric shape. The peak assignments were performed basing on the data reported earlier (see, e.g., [12, 13]).

The sheet resistance was measured in the temperature range from 77 K to 300 K by the standard ac (20 Hz) four probe method in the van der Pauw geometry with using silver paste contacts. The distance between contacts in our measurements was approximately equal to 3–4 mm.

3. Results and Discussion
A typical microphotograph of a copper substrate surface with a graphene layer on the top is shown in figure 1 (a). As it is known, an optical visualization of graphene synthesized on a copper substrate can be easily achieved by post-synthesis annealing in air at a temperature of about 200°C. This leads to an oxidation of copper that is not covered with graphene and, as a result, to a distinct optical contrast [14]. In figure 1 (a), the graphene layer is continuous, fully repeating the copper surface relief. The graphene layer transferred to Si/SiO$_2$ is presented in figure 1 (b). The inset shows an isolated graphene island allowing to evaluate the graphene grain size, which is equal to 30–40 µm.
Figure 1. The optical images of as-synthesized graphene on a copper substrate (a) and graphene transferred onto a Si/SiO₂ substrate (b). Inset: an island of graphene.

High resolution XPS spectra of graphene transferred to Si/SiO₂ before and after annealing at \( T = 750^\circ\text{C} \) are shown in figure 2. There are at least 4 components distinguished in the C1s core level spectrum, among them are \( sp^2 \)-hybridized graphitic carbon (at about 284.2 eV), \( sp^3 \)-hybridized carbon (at about 284.9 eV), and peaks corresponding to the bonding energies of species in functional groups adsorbed on graphene from the ambient atmosphere or during the transfer procedure. As seen in figure 2 (d), the peaks attributed to carbon bounds to oxygen disappear completely after sample annealing and the intensity of the \( sp^2 \) peak becomes higher. This indicates that annealing leads to a cleaning of the graphene surface from adsorbed contaminations resulted from their interactions with hydrogen and the formation of volatile products. The simultaneous increase in the intensities of the Si2p and O1s peaks (see figure 2 (e), (f)) indicates a considerable thinning of the coating on the Si/SiO₂ surface.

Figure 2. High resolution C1s (a, d), O1s (b, e), and Si2p (c, f) XPS spectra of graphene on the Si/SiO₂ substrate before (a – c) and after (d – f) annealing at 750°C in H₂+Ar atmosphere for 30 min.
Let us now consider the results obtained by the resistance measurements. Figure 3 shows typical temperature dependences of the sheet resistance of our CVD graphene samples, as well as the variation of the $\frac{d\rho}{dT}$ value with temperature. The room-temperature value of the sheet resistance for all the samples is in the interval of 1–1.5 kΩ/sq. For most of our as-transferred samples, the $\rho(T)$ dependence measured at the macroscopic scale is metallic-like (see results for sample #1 in figure 3 (a)). With decreasing temperature, the resistance decreases weakly over the whole investigated temperature range with an almost unchanged temperature derivative (excluding temperatures lower than 100 K, see figure 3 (b)). Such a resistance behavior coincides well with that obtained for CVD graphene when measuring at the micron scale [10, 11]. Thus, the granular sample structure (see insert in figure 2) influences insignificantly the conduction process, if any, that confirms a good quality of our CVD graphene samples. The resistance of the annealed sample also demonstrates a metallic-like behavior but with a higher slope of the $\rho(T)$ dependence. Obviously, like the case of the observed modification of the XPS spectrum, this is a result of an improved graphene layer quality due to the annealing influence on the previously adsorbed contaminations on its surface. However, the $\rho(T)$ change under annealing indicates additionally that these contaminations affect directly the conduction process in graphene samples.

For some samples, the resistance decreases with decreasing temperature at high temperatures but rises at low temperatures with a continuously increasing slope (see results for sample #2 in figure 3). In such cases, in the low temperature range the $\rho(T)$ curves can be fitted well by simple exponential functions. However, the calculated activation energy $E_a$ is found to be extremely small (for example, for sample #2 $E_a = 2.7$ meV). In our opinion, such a resistance behavior can be attributed not to the grain boundary influence but rather to the effect of chemical and structural defects formed during the synthesis and transfer process. In other words, in case of sample #2 we can observe the same direct effect of contaminations on the conduction process as discussed above for as-transferred and annealed sample #1 but the extent of their influence is higher that can be related to slight changes in the sintering and/or transfer processes.

In order to check this assumption, we have measured the high resolution C1s XPS spectra for the samples demonstrating a non-metallic $\rho(T)$ dependence. The results obtained for sample #2 are shown in figure 4 (a). One can see that the component of spectrum attributed to the C-OH or C-O-C bounds has a higher intensity as compared to the samples demonstrating a metallic-like resistance behavior (see figure 2 (a)). This gives strong grounds to state that it is these groups that result in the observed resistance behavior. Moreover, as seen in figure 4 (b), analogously to the case of sample #1 the additional annealing of sample #2 at 450°C in H$_2$+Ar atmosphere for 30 min leads to a reduction of the corresponding peak thus pointing to a decrease in the amount of carbon-based functional groups on
the sample surface but they are still existing in the annealed sample. This finding correlates well with the observed change of the $\rho(T)$ dependence under annealing. Indeed, as seen in figure 3, the annealed sample demonstrates a transition to an activation-type temperature dependence of the resistance at a lower temperature as compared to the as-transferred sample and the slope of the $\rho(T)$ curve increases with decreasing temperature much weaker (the corresponding activation energy is equal to $E_a = 0.7$ meV, i.e. four times less).

Thus, for both types of the $\rho(T)$ dependences obtained on our CVD graphene samples, we can see the analogous positive effect of an additional annealing on their chemical composition and electrical properties.

4. Conclusion
In summary, in this paper we present the results of the comparative study of the high resolution XPS spectra and the temperature dependences of the resistance for the graphene samples synthesized using the CVD technique and then transferred onto the nonconductive Si/SiO$_2$ substrates. According to the XPS data, our as-transferred graphene samples can be characterized by the existence of functional groups adsorbed on the surface. These adsorbed contaminations affect directly the conduction process in graphene samples. Nevertheless, we were able to produce graphene layers of a large area and a good quality that is confirmed by a high value of the conductivity and a metallic-like behavior of the resistance measured at the macroscopic scale. It was also shown that the sample annealing in a mixture of H$_2$ and Ar at $T = 250$–$750$°C results in a cleaning of the graphene surface from adsorbed contaminations and in a modification of the $\rho(T)$ dependence which demonstrates a higher slope in case of a metallic-like behavior for the as-transferred sample and a suppression of the activation-type dependence in case of a non-metallic one. Thus, changes in the chemical composition and electrical properties of transferred CVD graphene correlate with each other and an additional annealing in the H$_2$+Ar atmosphere can be proposed as a way to improve the graphene sample quality.

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