Effect of hydrogen concentration on CVD synthesis of graphene

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Abstract. The paper is devoted to the study of AP-CVD synthesis of graphene on a copper substrate. In this work, the effect of hydrogen concentration in the synthesis gas mixture on the growth of a graphene coating is studied experimentally. Two series of experiments with methane concentrations of 0.02% and 0.05% are presented. It is shown that a change in concentration of hydrogen has a nonmonotonic effect on the degree of substrate covering with graphene. This indicates that hydrogen is involved in several competing processes. One of these processes is stabilization of the edges of growing graphene domains. Another is etching of the forming graphene structures and reduction of hydrocarbon radicals on the copper substrate surface and in the bulk. It is shown that an increase in methane concentration leads to an increase in the rate of graphene crystal growth. To preserve the kinetics of graphene domain growth, it is necessary to reduce the H2/CH4 coefficient in the working mixture.

1. Introduction
Graphene is a layer of carbon atoms, tightly packed in a honeycomb structure [1]. It attracts great interest due to its outstanding mechanical, thermal, electrical and optical properties [2-4]. They make it suitable for a wide range of applications in such areas as flexible electronics, spintronics, catalysis, composite materials, energy storage and conversion, etc. [5-9]. The method of chemical vapor deposition (CVD) on copper substrates is the most promising approach to the production of high-quality graphene films that can be scaled [10]. During CVD synthesis on the copper surface, graphene nucleation sites appear due to decomposition of a carbon precursor; then these domains grow and turn into a continuous polycrystalline film [11]. The size of crystalline graphene fragments of the film is an important parameter, which largely determines the film properties [12]. Understanding the kinetics of CVD synthesis of graphene is important to accelerate the process of graphene layer production and achieve better control of its properties. Growth dynamics depends strongly on such parameters as synthesis temperature, substrate morphology, pressure and composition of the gas mixture [13, 14]. Hydrogen has a great influence on the following processes and characteristics: synthesis of graphene, reducing pollution and defects of the substrate surface; an increase in the copper grain size during annealing [15, 16]; shape of graphene domains [17–19]; nucleation of graphene nuclei on a catalytic substrate [20]; and number of the forming graphene layers [21]. This studies the effect of hydrogen concentration in a synthesis mixture on formation of graphene on the copper surface.
2. Experimental section
Synthesis was carried out on AlfaAesar 99.8% copper foil with a thickness of 25 μm. The synthesis chamber (0.5 liter volume) is a quartz tube placed in a furnace that can be shifted to remove the sample from the hot zone quickly. A mixture of Ar, H₂ and CH₄ gases was fed through flowmeter-regulators, creating a flow in the synthesis chamber. The copper substrate was placed in the synthesis chamber. Then, the chamber was evacuated, filled with Ar, and heated to the annealing temperature of 1070°C. The substrate was annealed for 30 min in the H₂ atmosphere. Immediately after annealing, a mixture of Ar + H₂ + CH₄ gases was supplied to the chamber for the synthesis. The flow rate of Ar was chosen in such a way that the total flow rate was (111 sccm). In the first series of experiments to achieve the flow rate of CH₄ gas of 0.022 sccm (0.02% of the total flow rate), the flow rate of H₂ was 5, 10, and 15 sccm (4.5, 9, and 13.5%); the synthesis time was 10 min. In the second series of experiments, to achieve the flow rate of CH₄ gas of 0.055 sccm (0.05%), the flow rate of H₂ was equal to 10, 15 and 20 sccm (9, 13.5 and 18%); the synthesis time was 10 minutes. To determine the number of layers, the method of Raman spectroscopy (RS) was used. The Raman spectrometer T64000 Horiba JobinYvon with a wavelength of exciting radiation of 514.5 nm was used for the research. The size of graphene domains and degree of copper coverage were analyzed using optical microscopy (by Olympus BX51M) with oxidation of a substrate.

3. Results and discussion
The optical images of the copper substrate surface oxidized in air after graphene synthesis are shown in Fig. 1. The optical images show that a change in H₂ concentration has a nonmonotonic effect on the degree of graphene coating of the substrate and, accordingly, the synthesis rate. For both series of experiments, the maximum degree of coating is observed at medium concentrations of H₂. Namely, for CH₄ concentration of 0.02% is observed with H₂ of 9%, and for CH₄ of 0.05% is observed with H₂ of 13.5%. Moreover, with an increase in H₂ concentration, the size of graphene domains decreases, and with a decrease in H₂ concentration, the domains lose their distinct form, and the coating takes a net appearance. In the Fig. 1b, the surface of the substrate is completely covered with graphene, but there are many black dots showing defective spots in graphene. This shows that a change in hydrogen concentration affects several processes occurring during the synthesis.
Figure 1. Optical images of the copper substrate surface oxidized in air after the graphene synthesis. Light yellow areas correspond to non-oxidized copper coated with graphene. Sample was synthesized with CH<sub>4</sub> flow rate of 0.022 and H<sub>2</sub> 5 sccm (corresponds to 0.02% and 4.5% of the total flow rate) (a); CH<sub>4</sub> 0.055 and H<sub>2</sub> 10 sccm (0.05% and 9%) (b); CH<sub>4</sub> 0.022 and H<sub>2</sub> 10 sccm (0.02% and 9%) (c); CH<sub>4</sub> 0.055 and H<sub>2</sub> 15 sccm (0.05% and 13.5%) (d); CH<sub>4</sub> 0.022 and H<sub>2</sub> 15 sccm (0.02% and 13.5%) (e); CH<sub>4</sub> 0.055 and H<sub>2</sub> 20 sccm (0.05% and 18%) (f).

In the process of synthesis on the surface of catalytic copper substrate under the action of high temperature, CH<sub>4</sub> decomposes in the presence of H<sub>2</sub> co-catalyst (adatoms of H) into the CH<sub>x</sub> and H radicals, x<4. Then, these CH<sub>x</sub> radicals are decomposed into atomic C or recombined into C<sub>2</sub>H<sub>x</sub> dimers (1).

\[ \text{CH}_4 \xrightarrow{\text{Temp, Cu, } H_2} C_yH_x + (4 - x)H, x < 4, y = 1, 2 \]  

(1)

As a result, the following elements exist on the copper surface (H, C, CH, CH₂, CH₃, CH₄, C₂H, C₂H₂, and C₂H₂), [22-24]. Most of these reactions are reversible and a change in hydrogen or methane concentration will shift the equilibrium in one or another direction. An increase in methane concentration increases the flow of carbon to the places of graphene structure growth, and the rate of synthesis increases (Fig. 1 b and c; d and e). At high concentrations of hydrogen, the etching of the forming graphene structures is enhanced. That is, when the amount of hydrogen becomes too much, the reaction of hydrogenation of individual particles becomes dominant, and chemical equilibrium shifts to etching through desorption of hydrogenated particles into the gas phase [25].
In addition, with the growth of a graphene crystal, the atoms located at the boundary have dangling bonds and can interact either with hydrogen from the gas phase or with the atoms of substrate. According to calculations in [24], the edges of a graphene domain, passivated by the atoms of a copper substrate, can be etched much easier than the edges, passivated by the hydrogen atoms. It is stated in [24] that the catalytic effect of hydrogen consists in stabilization of the edges of growing graphene domains. Such a catalytic effect has a limitation. An increase in hydrogen concentration up to a certain point leads to saturation, that is, almost all atoms at the edges are passivated by hydrogen. A further increase in hydrogen concentration will not affect this process, but will only reduce concentration of carbon-containing fragments and accelerate the etching of the resulting graphene domains. Thus, at low concentrations of hydrogen, it is not enough to stabilize the edges of domains. That is consistent with the data of our experiment. Namely, with the fact that with a decrease in hydrogen concentration, the rate of synthesis decreases. Thus, an increase in concentration of methane has almost no effect on the process of saturation of the graphene domain edges with hydrogen, changing only the rate of etching and growth of the graphene layer. The net-like, non-uniform form of graphene coatings (Fig. 1 a, b) is acquired due to passivation of domain edges by the atoms of substrate. In this case, the defects, microrelief, orientation and boundaries of the copper substrate grains lead to formation of defects and boundaries of the growing graphene layer.

In literature, to describe the synthesis mixture composition, various ways are use: they indicate the absolute value of gas flow rates, partial pressure of gases in the mixture or the coefficient of their ratio. This is important to consider when comparing data. In this paper, if we consider the \( \text{H}_2/\text{CH}_4 \) volume ratio, then the maximum growth rate for \( \text{CH}_4 \) of 0.02% is achieved with a coefficient of 450, and for \( \text{CH}_4 \) of 0.05%, this coefficient is 270. In the previous work [26], under similar synthesis conditions, for \( \text{CH}_4 \) concentration of 0.1%, the maximum synthesis rate was reached at \( \text{H}_2/\text{CH}_4 \) vol. ratio of 180. Thus, to achieve the maximum synthesis rate with an increase in \( \text{CH}_4 \) flow rate, it is also necessary to increase the \( \text{H}_2 \) flow rate, but the \( \text{H}_2/\text{CH}_4 \) vol. coefficient is not maintained. Many factors influence the synthesis of graphene, such as methane decomposition, etching, passivation and stabilization of the edges of the growing graphene domains with hydrogen. Therefore, the \( \text{H}_2/\text{CH}_4 \) vol. ratio, which provides the maximum growth rate of graphene, varies nonmonotonically with an increase in the concentration of \( \text{CH}_4 \).

The RS analysis of samples (Fig. 2) showed that the individual domains are single-layered, and for the samples where the coating becomes continuous, a signal from two to three layers is characteristic. We assume that under our synthesis conditions, individual domains during their growth overlap each other, when reaching the neighboring borders. The model of “inverted wedding cake” for the graphene growth is recently discussed in literature. According to this model, in the nucleation site, which can be a defect of copper surface or a place of critical carbon concentration, the first layer of graphene is initially formed and grows. If hydrogen concentration on the copper surface is not sufficient, then the edges of the growing graphene domain are passivated by the substrate atoms, and this prevents penetration of the carbon fragments under the first layer, and the growth occurs only on it. If hydrogen is sufficient, then the edges of the graphene domain are passivated by hydrogen atoms, while the carbon fragments can penetrate under the first layer and the growth of the second and subsequent layers begins from the nucleation center [25]. Moreover, the growth rate of the second and subsequent layers differs from the first layer, since different synthesis conditions are created between the copper surface and the first layer of graphene, as in a separate micro-CVD chamber. It is assumed in [27] that this process can be suppressed by oxidizing the copper substrate surface before the direct synthesis. In this case, diffusion of carbon fragments over the copper surface will be impeded, and only one layer of graphene will be formed, and the growth rate should be decreased.
Figure 2. RS spectra (normalized to the G line and shifted in height by 50 units relative to each other) of samples synthesized at CH$_4$ flow rate of 0.02% and H$_2$ of 4.5%, 9%, 13.5% (a); CH$_4$ flow rate of 0.05% and H$_2$ of 9%, 13.5%, 18% (b).

Conclusion
It was experimentally shown that the influence of hydrogen in a mixture is determined by two main processes. The first is the growth and etching of graphene structures due to interaction with the products of methane and hydrogen dissociation. The rates of these processes are determined by the ratio of methane to hydrogen concentrations in the synthesis mixture. The second process is passivation of the growing graphene layers by hydrogen atoms, which weakens interaction with the copper catalytic substrate. This process depends on the partial pressure of hydrogen. A change in the degree of passivation of graphene domains by hydrogen atoms leads to a change in the dynamics of graphene layer growth and etching. Thus, at various partial pressures of hydrogen, the optimal conditions for the growth of graphene layers are achieved at different CH$_4$/H$_2$ vol. ratios.

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