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Chemical vapor deposition growth of graphene on copper substrates: current trends

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Abstract. The most interesting recent developments and trends in graphene growth technologies on copper substrates are reviewed. An analysis is given of how the substrate preparation quality and other process parameters affect the properties of films obtained at different pressures and temperatures on a copper foil and lower-thickness copper films. The fabrication methods and properties of large single-crystal graphene domains are discussed together with technologies that do not require graphene film transfer onto a dielectric substrate. Another important possible approach, that of graphene growing laterally from specially formed few-layer graphene and carbon-containing seeds or metal catalysts, is also discussed.

1. Introduction

The growing interest in studying graphene is connected with the expectation of the revolutionary role it can play in electronics, mechanics, optics, and other fields of science and engineering [1, 2]. All over the world, the activity of many scientific groups is being directed toward creating and studying graphene; thousands of studies devoted to graphene are published each year. In spite of the chemical simplicity and smallest possible thickness (equal to one atom), graphene is an extremely strong material possessing high conductivity (four times greater than that of copper) and a very high mobility of charge carriers (up to 10^6 cm^2 V^{-1} s^{-1} at low temperatures, and up to 2×10^5 cm^2 V^{-1} s^{-1} at room temperature [3, 4], which is more than two orders of magnitude higher than the mobility of carriers in silicon and 20 times greater than that in GaAs). Therefore, graphene is an ideal material for high-speed electronics, photonics, and many other fields. In particular, graphene is considered a promising candidate for the essential addition to and even replacement of silicon technology. Its strength, conductivity, and transparency represent an excellent combination promising for a wide spectrum of applications.

A practical implementation of graphene requires the development of technologies for growing graphene samples of a large area and high quality. There are several approaches to producing graphene, the most important of which are the epitaxial growth of graphene on SiC substrates [5] and synthesis by the method of chemical vapor deposition (CVD) on metallic substrates [6, 7]. In recent years, it is this CVD growth on metallic substrates that is considered to be the most promising, and the growth on copper substrates is considered to be the most encouraging variant of the CVD synthesis of graphene. B H Hong [8] (Samsung, South Korea) has described a method of producing graphene with its transfer onto silicon wafers with a diameter of 30 cm with 98% coverage, and also onto flexible polymeric substrates. T Kobayashi et al. [9] (Sony, Japan) have demonstrated transparent films of graphene with a length of 100 m and a resistivity to 150 Ω/sq on flexible substrates. But the cost of this material is still high and its quality, or that of some of its parameters, is not always satisfactory. Thus, the mobility of charge carriers in graphene fabricated on flexible substrates, according to Ref. [9], is only 600–900 cm^2 V^{-1} s^{-1}. Therefore, work on the development of different methods of growing graphene is actively continuing all over the world.

In principle, the CVD methods of growing graphene were developed several years ago [3, 10, 11]; however, the main disadvantage of these films was their polycrystalline structure consisting of small single-crystal blocks (which were conventionally called domains). As a result, these films possessed

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a resistivity from 0.8 to several kΩ/sq, and the mobility of charge carriers after the transfer onto a SiO_2/Si substrate varied from 600–800 to 2000–3000 $cm^2\ V^{-1}\ s^{-1}$ [10, 11]. Such films did not make it possible to attain and utilize one of the basic attractive properties of graphene, namely, the high mobility of charge carriers. As noted above, the values of mobility in graphene at room temperature can reach 200,000 $cm^2\ V^{-1}\ s^{-1}$ [1, 4]. In this review, we consider the latest achievements and trends in the development of the technologies of graphene growth by CVD methods on copper substrates, which are directed, first of all, toward obtaining large domains of graphene and, as a result, of a material with higher quality characteristics.

2. Selection and preparation of a metallic substrate

Metals that are characterized by a low carbon solubility are usually employed as substrates, such as Cu, Ni, Co, Fe, Ir, and Ru [12]. From these, only Co, Fe, Cu, and Ni have a relatively low cost, thus presenting the most promising materials from the viewpoint of growing graphene samples of a large area for real industrial applications. There is one more important parameter that should be taken into consideration when choosing the material for a substrate. Because of the high C–H binding energy (440 kJ mol^{-1}) in the methane molecules used for film growth, their decomposition occurs at a high temperature (more than 1200 °C). This temperature can be reduced by using catalysts. It is just the metallic substrates that can serve as catalysts. Ni, Co, and Fe are sufficiently strong catalysts; therefore, they are unsuitable for use as substrates, since, in this case, it is difficult to control the thickness of the growing film. Thus, the saturation of 50-μm nickel foils by carbon at 1000 °C makes it possible to obtain a graphite film several micrometers thick upon cooling [13]. Copper exhibits both a low carbon solubility ($< 0.001\%$) and a relatively weak catalytic action on methane, thus ensuring a low concentration of carbon atoms on the surface and, correspondingly, a thin growing layer. Note also the high selectivity of etchants utilized for etching copper, and also the fact that no carbides are formed on the copper surface. The totality of these factors makes copper the most promising substrate for growing graphene.

No less important for growing graphene is the appropriate preparation of the substrate surface, i.e., obtaining a sufficiently smooth and defect-free surface. This can be provided by different methods. One of the most widely utilized involves a preliminary annealing of the substrate in an $Ar + H_2$ mixture at a temperature of 900–1080 °C for 30–40 min (see, e.g., Ref. [14]). A typical scheme for growing graphene by the CVD method with preliminary annealing is given in Fig. 1. The annealing leads to a flattening of the surface and coarsening of grains of the copper substrate. Another (as a rule, additional) method of preparing a substrate includes electropolishing [15]. The Alfa Aesar GmbH (Germany) produces at present a copper foil with a thickness of 25 μm (which is optimal for growing graphene) and with a sufficiently smooth surface, which does not require additional electropolishing. In recent years, it is precisely this foil that has been used most frequently for growing graphene sheets.

The above preparation of the surface decreases its relief, but does not eliminate the surface defects completely. In addition, on the surface there are traces of atomic planes, grain boundaries, etc., since the metals are polycrystalline. It is precisely such regions that serve as centers of nucleation for the growing film. Figure 2 (taken from Ref. [16]) shows a scheme of nucleation upon the growth of graphene, an image of the surface with the domains grown, and the spectra of Raman scattering taken from different regions of the surface. It can be seen that the film is thicker in the regions of surface defects.

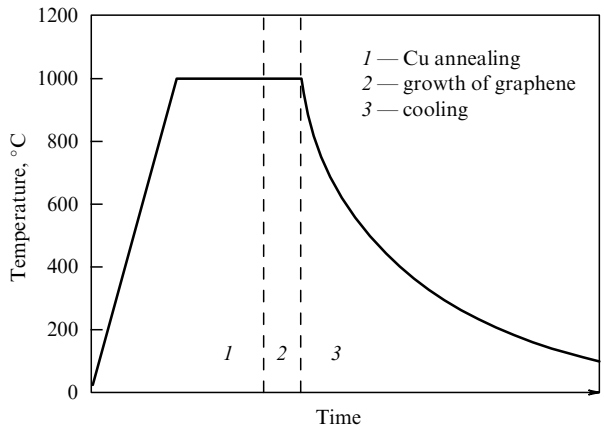

Figure 1. Typical regime of growth of graphene, including a stage of preliminary annealing in an Ar atmosphere with the addition of hydrogen (schematic).

One more important factor that affects the growth rate is the orientation of the substrate. This is related to the different catalytic activity of surfaces of different orientations. It is important that the preliminary annealing of the substrate lead to a reconstruction of atomic distribution over the surface and to the common orientation of all the atoms on the surface and, as a results, to the equalizing of the growth rate and of the thickness of the grown film. The presence of impurities in the copper substrate sharply increases its catalytic activity. All other growth conditions being equal, the increase in the content of impurities (to the levels of 98.9 and 99.99% [16]) leads to an increase in the number of grown layers.

The best results have been obtained by growth on a thin copper foil ($\sim 20-25$ μm) [16]. It has been shown that the thinner copper layers lead to an island-like growth of graphene, while thicker layers lead to an increase in the inhomogeneity of the film thickness.

In addition, for growing graphene, copper layers deposited on various substrates, e.g., SiO_2/Si, silicon/tungsten, or a polymer film, are also used [17].

3. Growth on copper substrates: examples of growth and a comparison of the results

3.1 Growth at temperatures lower than the melting point of copper

3.1.1 CVD at atmospheric pressure. The process of growth at atmospheric pressure is used relatively rarely. The characteristic temperatures of growth are 800–1000 °C, while the characteristic times last for 10–15 min [15, 18]. It is necessary to note the relatively low mobility of carriers in the materials grown by this method. Details of the growth regimes used in these articles are collated in Table 1. The authors of Ref. [19] proposed a method of growing graphene sheets with the use of

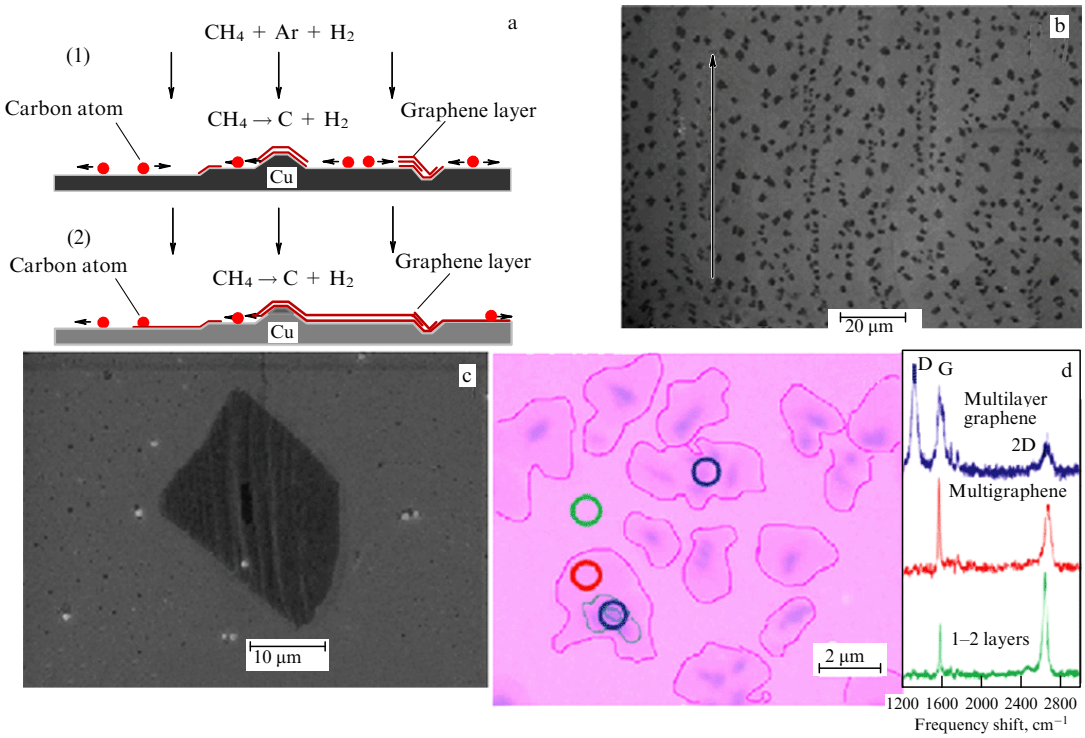

Figure 2. (a) Scheme of the nucleation in a graphene growth, (b) image of the surface with grown domains (the arrow indicates the direction of atomic steps), (c) image of a single domain, and (d) Raman spectra taken from different sites on the surface [16].

gas burners [with a mixture of CH_4 and H_2 taken in a ratio of 1 : (5 – 20)]. It turned out that the films with a thickness of 2–8 layers and with a high resistivity equal to 40 kΩ/sq are thus obtained.

In recent years, two-stage technologies have been actively developed that use the method of slow growth for the formation of a low concentration of growth nuclei, their enlargement during the first stage, and then their rapid overgrowing of the entire remaining area with the formation of a continuous film at the second stage. This approach, realized for a film growth at the ambient pressure in Refs [20, 21], gives sheets with a high percentage of graphene (95%); the area of the domains reaches almost 300 μm^2, and the sheets possess relatively low resistivity (710 Ω/sq).

3.1.2 CVD at a reduced pressure or in a high-vacuum chamber. In Ref. [16], the concentration of methane (flow rate of 30 cm^3 min^{-1}) was selected at which graphene predominates on the plate (90%). In work [17] by the same authors, a pulsed mode of annealing was proposed. In this case, the coverage of the surface by graphene depends on the number of heating pulses. Eight pulses correspond to 0.8 monolayers of graphene on the surface. Measurements by the Raman spectroscopy method have shown that such films contain a large concentration of defects.

Graphene domains of large sizes (125–200 μm) have been obtained in Refs [17, 22, 23]. The measurements of the mobility of charge carriers inside one domain give a high value (for the grown graphene) of 16,000 cm^2 V^{-1} s^{-1} [22] (see also Table 1); note, however, that the authors of Ref. [22] used two-stage growth, when separate large domains of graphene are grown at the first stage, and at the second (short-term) stage the regions between the large domains become grown-in, producing a continuous film. In the case of smaller graphene domains, or when the size of the tested region includes several domains, the mobility of charge carriers decreases to ~ 4000 cm^2 V^{-1} s^{-1} [12, 17]. On the whole, the above-marked tendency of the growth of separate coarse grains of graphene has been widely accepted in the last two years. Thus, the authors of Ref. [24] discuss the conditions for a growth of large single-crystal 'flowers' of graphene up to 100 μm in size with four or six lobes, depending on the selected methane-to-hydrogen ratio.

Figure 3 shows the shape and size of graphene domains growing on a copper substrate, which depend on the pressure in the growth chamber and the methane-to-hydrogen ratio (borrowed from Ref. [24]). After the transfer onto the Si/SiO_2 substrate, the mobility of charge carriers in the graphene was on the average ~ 4200 cm^2 V^{-1} s^{-1}, and on the substrate made of hexagonal boron nitride it was approximately 20,000 cm^2 V^{-1} s^{-1}. Note also the absence of the peak D in the Raman spectra, which indicates a high quality of the graphene domains. Record-high values of the sizes of graphene domains and of the mobilities of charge carriers in them have been obtained in Refs [13, 25]. The size of single-crystal domains of graphene grown on copper reached 250 μm (Fig. 4). This material showed low sheet resistivity, 120 Ω/sq, and the mobility of charge carriers inside single domains was 17,000–25,000 cm^2 V^{-1} s^{-1} on an SiO_2/Si substrate, and 27,000–45,000 cm^2 V^{-1} s^{-1} on an h-BN layer deposited on an SiO_2/Si substrate.

The high flow rates of hydrocarbons make it possible to overcome the self-restrictions of graphene growth on copper and to controllably grow, for example, bigraphene and thicker layers. Such layers of few-layer graphene with high characteristics are important and necessary for a wide spectrum of applications. Thus, Lee at al. [26] adopted regimes suitable for growing bigraphene. The size of the bigraphene film grown at 1000 °C [26] reached 4 × 4 cm, and 98% of all transistors created on this sample had an energy

Table 1. Methods and conditions of growing graphene (according to various studies).

Growth method	Growth conditions	Characteristics of layers*	References
AP-CVD	$H_2 : Ar = 10 : 600$ cm^3 min^{-1}, 1000 °C CH_4, 41 ppt, 10 min	95% graphene, 50-μm domains, 400–600 cm^2 V^{-1} s^{-1}	[15]
AP-CVD	$H_2 : Ar = 20 : 100$ cm^3 min^{-1}, 800 °C $CH_4 = 60$ cm^3 min^{-1} ($NH_3 = 60$ cm^3 min^{-1}), 10 min	2 – 6 layers, 300–1300 cm^2 V^{-1} s^{-1}, 200–450 cm^2 V^{-1} s^{-1} (N-alloyed)	[18]
AP-CVD	1050 °C, 1st stage of growth: $H_2 : CH_4 : Ar = 20 : 15 : 1465$, CH_4 5 ppm, 20 min, and 2nd stage of growth: $H_2 : CH_4 : Ar = 20 : 165 : 1315$, CH_4 55 ppm, 15 min	95% graphene, domains to 290 μm^2 in area, 710 Ω/sq	[20]
AP-CVD	1120 – 1160 °C, $CH_4 = 6$ cm^3 min^{-1} $H_2 = 300$ cm^3 min^{-1}, 0.5–4 h	Separate domains, 400–600 Ω/sq, growth rate of domains is 10–50 μm min^{-1}	[28]
LP-CVD	900 °C, total pressure < 40 mTorr, $CH_4 = 30$ cm^3 min^{-1}, $H_2 = 100$ cm^3 min^{-1}	90% graphene, 13–51 kΩ/sq, 4050 cm^2 V^{-1} s^{-1}	[13]
HV-CVD	1000 °C, total pressure 10^{-5} Torr, C_2H_4 separate pulses	Eight pulses yield 0.8 layer of graphene. Numerous defects	[17]
LP-CVD	1035 °C, total pressure 160 mTorr, 1st stage of growth: $CH_4 = 7$ cm^3 min^{-1}, $H_2 = 2$ cm^3 min^{-1}, 30 – 40 min, and 2nd stage of growth: $CH_4 = 35$ cm^3 min^{-1}, $H_2 = 2$ cm^3 min^{-1}, 2–3 min	90% graphene, size of domains is 142 μm^2, 1000–16,000 cm^2 V^{-1} s^{-1}	[22]
LP-CVD	1000 °C, total pressure 80–400 mTorr, $CH_4 : H_2 = 1 : (2–30)$ cm^3 min^{-1}, 40 min	Separate domains to 100 μm in size, 20,000 (h), 10,000 (e) cm^2 V^{-1} s^{-1} on h-BN, $\sim$ 4200 cm^2 V^{-1} s^{-1} on SiO_2	[24]
LP-CVD	1035 °C, total pressure 17 mTorr, $CH_4 = 0.5 – 1.3$ cm^3 min^{-1}, $H_2 = 2$ cm^3 min^{-1}, 10–90 min. Growth rate of domains is 6 μm min^{-1}	Separate domains to 250 μm in size, 17,000–25,000 cm^2 V^{-1} s^{-1} on SiO_2/Si, 27,000–45,000 cm^2 V^{-1} s^{-1} on h-BN	[25]
LP-CVD	1000 °C, total pressure 0.35 Torr, $CH_4 = 70$ cm^3 min^{-1}, $H_2 = 100$ cm^3 min^{-1}	Bigraphene, 580 cm^2 V^{-1} s^{-1}	[26]
LP-CVD	1050 °C, total pressure 5 Torr, $H_2 : CH_4 = 10 : 500$, 40 min, $Ar + H_2 = 500$ cm^3 min^{-1}	90% bigraphene, 1300–4400 (h), 1400–3000 (e) cm^2 V^{-1} s^{-1}	[27]
LP-CVD	300 – 600 °C, total pressure 100 Torr, 1st stage of growth: toluene 2.7 ml h^{-1} (300 mTorr), 60 min, and 2nd stage of growth: 3000 mTorr, 5 min	Graphene, continuous film, 8 kΩ/sq, 810 (h), 190 (e) cm^2 V^{-1} s^{-1}	[21]
LP-CVD	1000 °C, 700 nm Cu on quartz, He = 1000 cm^3 min^{-1}, $H_2 = 50$ cm^3 min^{-1}, $H_2 : CH_4 : He = 15 : 50 : 1000$, 5 min	1–2 monolayers, 1100 (h), 550 (e) cm^2 V^{-1} s^{-1}	[30]
LP-CVD	1000 °C, total pressure 100–500 mTorr, 100 – 450 nm Cu/Si, $H_2 : CH_4 = 6 : 100$, 15 min–7 h	Graphene	[31]
LP-CVD	1000 °C, total pressure 11 Torr, 500 nm Cu, $H_2 = 50 – 200$ cm^3 min^{-1}, $H_2 : CH_4 = 23 : 100$, 10 – 20 min	> 93% graphene, 700 (e) cm^2 V^{-1} s^{-1}	[32]

* Among other parameters, the table contains the resistivities of the layers (in Ω/sq) and the mobilities of charge carriers (in cm^2 V^{-1} s^{-1}) on (by default) an SiO_2/Si substrate; (h) and (e) stand for the mobilities of holes and electrons, respectively.
AP-CVD stands for CVD at atmospheric pressure; HV-CVD — CVD in a high vacuum, and LP-CVD — CVD at a lowered pressure.

gap equal to 250 meV. The mobility of charge carriers in this material proved to be small (580 cm^2 V^{-1} s^{-1}). The higher growth temperature (1050 °C [27]) made it possible to obtain higher values of mobility for bigraphene: 1300–4400 cm^2 V^{-1} s^{-1} for the holes, and 1400–3000 cm^2 V^{-1} s^{-1} for the electrons. Bigraphene composes 90% of samples with an area of 1.5 × 5 cm with the total coverage of the substrate being 99%.

In parallel with the high-temperature film growth, the technologies of growth at low temperatures (500–600 °C) are also under development at present [21]. In that work, the method of two-stage growth was applied again, focusing on the growth of separately located domains as large as possible and with the growing-in of the spaces between them. The defect-related D peak in the Raman spectra is visible, but its amplitude is low. Nevertheless, the adoption of low temperatures did not lead to good parameters of the films: the resistivity of such films proved to be high (see Table 1), and the mobility of the carriers was low.

3.2 Growth at temperatures higher than the melting point of copper

Interesting results have been obtained when using higher temperatures (higher than the melting point of copper) [28]. Figure 5 depicts the results of growth at temperatures of 1120–1160 °C and different flow rates of the component gases. The authors of Ref. [28] ascribe the formation of ordered arrays of domains of equal sizes to the possibility of minimizing the surface energy of graphene due to the motion of the domains over the surface and to the effects of their self-organization on the surface of the copper melt. The hexagonal shape of the nuclei favors their efficient joining and the

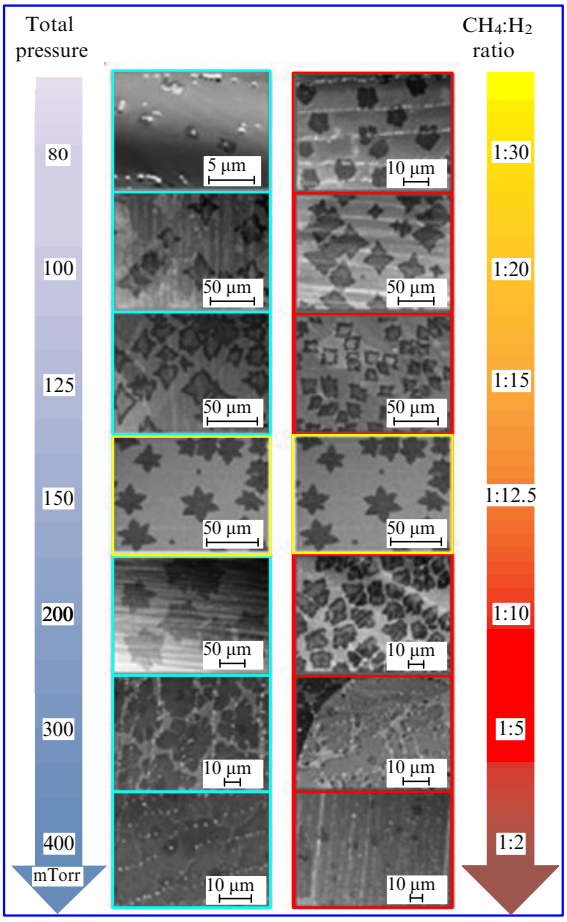

Figure 3. Variation of the shape and size of graphene domains growing on a copper substrate as functions of the pressure in the growth chamber and the relationship between the gas flows [24]. The left-hand panel corresponds to a methane-to-hydrogen ratio equal to 1:12.5; the right-hand panel corresponds to a total pressure of 150 mTorr.

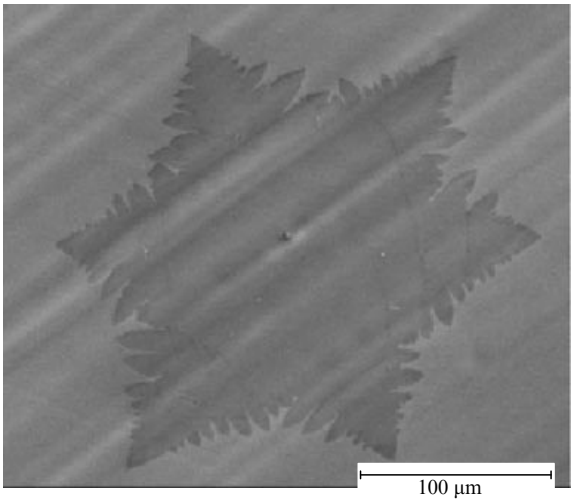

Figure 4. Image of a graphene domain with a size of 200 μm [25].

formation of a continuous film. The nucleation of graphene usually occurs in the defects of the substrate, such as grain boundaries, leading to inhomogeneities in the distribution and sizes of the domains. When using melts, the properties of the substrate become more uniform. Furthermore, the rate of growth of the domains does not usually exceed 1–10 μm min^{-1}. In Ref. [28], substantially higher rates of growth of the domains have been revealed, from 10 to 50 μm min^{-1}. The relationship between the 2D and G peaks in the Raman spectra indicates that precisely a monolayer is formed, and the absence of the D peak confirms the high quality of the graphene structure. The resistivity of these layers is sufficiently low (400–800 Ω/sq), which also testifies to a good quality of the graphene produced.

The authors of Ref. [29] suggested a method of obtaining graphene on molten copper or nickel substrates. The method is based on the growth of graphene or few-layer graphene during the cooling of the melt of a carbon-containing metal. The melting point of copper is 1083 °C. Because of the low solubility of carbon in copper, the maximum temperature of the process was varied from 1200 to 1500 °C, and the holding time at this temperature amounted for 16 h. By varying the maximum temperature and the amount of carbon in the melt, it is possible to control the thickness of the growing film from a single layer to several nanometers. The disadvantages of this method are the high temperatures and large duration of the process.

3.3 Methods of graphene production that do not require a transfer of the film onto a dielectric substrate

An interesting development of the above-considered methods is going to the use of thin copper films, in combination with the capturing of carbon atoms from the atmosphere of the chamber. This makes it possible to reduce the temperature of the process even to below 1083 °C, since the melting point of thin films is lower than the melting point of bulk materials. Thus, copper sheets 200–250 nm thick have a melting point of ~ 1060 °C. The duration of the process also decreases sharply. One more important advantage of this approach resides in the opportunity of utilizing traditional substrates: silicon or SiO_2/Si.

Study reported in Refs [30–32] should be added to the above-mentioned methods of graphene growth on a thin copper film, where the opportunity of the removal (sublimation) of the copper film from under the growing layer directly in the process of growth has been demonstrated. The fact that copper is evaporated in the chamber at temperatures of ~ 1000 °C and above is well known. The authors of Refs [30–32] have matched the thickness of the copper film and the times of the process of graphene growth so that, at the end of the process or somewhat later (after additional annealing), the copper film could be completely evaporated, after it has effected its catalytic action, and the graphene sheet proved to be located directly on the underlying dielectric substrate. In these studies, copper films with a thickness of 100–450 nm on a quartz substrate were used. A drawback of this approach lay in the fact that the deposited films usually had thickness inhomogeneities. As a result, the evaporation of the copper film also occurred nonuniformly, thus leading to a thickness inhomogeneity of the grown sheet.

Another developing area of the growth technology of graphene, which does not require its transfer to an insulating substrate, is its lateral growth from metallic catalysts located in a quasi-periodic manner on the surface. Thus, the authors of Refs [33–35] have shown the possibility of using nickel pads formed on SiO_2/Si substrates for this growth. The disposition of nickel pads at sufficiently close distances makes it possible to attain overlapping of graphene regions growing laterally from each of the pads. These nickel pads can be used as the

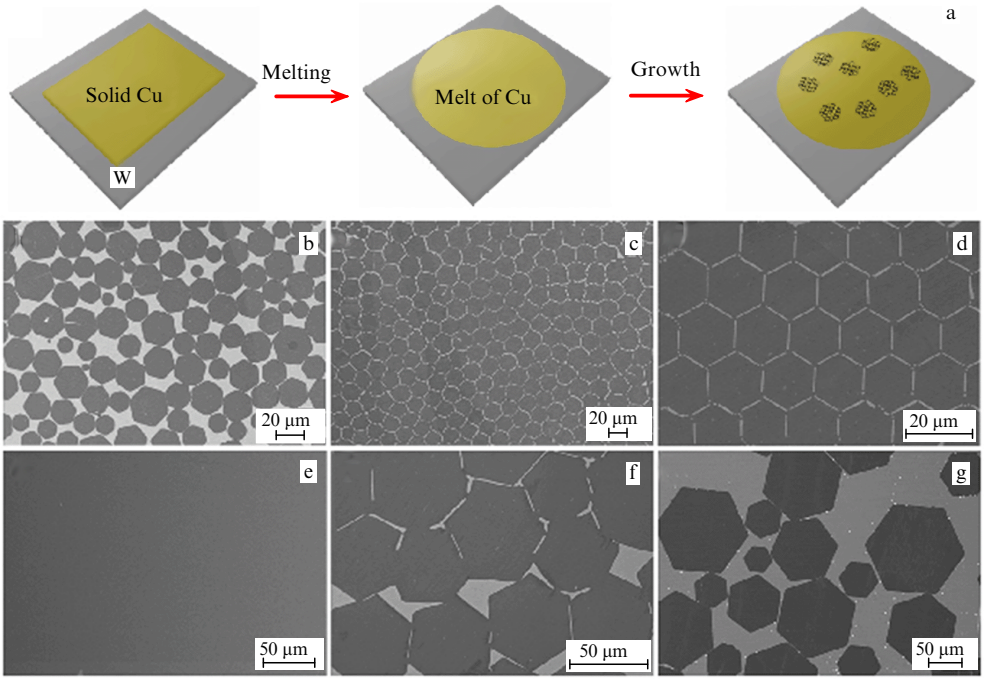

Figure 5. (a) Schematic of a graphene growth, including heating to a temperature exceeding the melting point of copper and subsequent growth. (b) SEM images of the copper surface with separate domains of graphene grown in a gas-mixture flow (6 cm^3 min^{-1} CH_4/300 cm^3 min^{-1} H_2) at 1120 °C for 30 min. (c, d) Evolution of the surface pattern with increasing growth time [(c) 38 min]. (e) Continuous graphene film obtained for 2 h. (f, g) SEM images of the copper surface with separate graphene domains grown in a gas-mixture flow (6 cm^3 min^{-1} CH_4/300 cm^3 min^{-1} H_2) at (f) 1140 °C and (g) 1160 °C for 30 min [28].

contacts for testing the properties of the obtained sheet. The sheets grown in this way demonstrate a low mobility of charge carriers (on the order of 100 cm^2 V^{-1} s^{-1} [33]). An important advantage of such sheet is the feasibility to vary the strength of the current by seven orders of magnitude by varying the voltage at the gate [33–35]. It should be noted that usually the strength of the current in graphene is modulated by the voltage at the gate only in narrow limits (a fewfold or, at best, an order of magnitude) [1, 36]. The possibility of changing the strength of the current by several orders of magnitude is very important for creating transistors. On the other hand, it is obvious that the films obtained in work [33–35] are, most likely, a chemically modified graphene, since they exhibit properties that are not typical of graphene.

On the whole, such approaches, which do not require the transfer of a film, are very promising, since the transfer of graphene is a sufficiently complex technological operation and, sometimes, it is precisely this operation that determines the final parameters of the sheet obtained. For instance, the use of polydimethylsiloxane (PDMS) leads, as a rule, to a high resistivity of the graphene sheet fabricated, and to low mobility of charge carriers because of contamination of the graphene [37, 38].

4. Influence of different parameters of the growth process on the quality and properties of graphene

4.1 Role of hydrogen present in the gas mixture used for growth

The role of hydrogen added in the process of graphene growth is analyzed in Ref. [21]. The authors of that study, who have acquired extensive experience in growing graphene [13, 14, 17, 22, 23], came to the conclusion that the shape of the growing domains is determined by the partial pressure of hydrogen in the process of graphene growth. It is assumed that hydrogen etches the edges of the growing domain, leading to simpler shapes of domains. The low ratios between the fluxes of hydrogen and methane lead to a complex shape of the growing domains (for example, 'flowers' with irregular edges). In Ref. [39], there are direct proofs of the possibility of utilizing annealing in hydrogen for the etching of the grown graphene. Moreover, observed was not only a decrease in the sizes of graphene islands, but also the appearance of hexagonal holes in the film, most likely, at the defect sites.

The authors of Ref. [40] revealed that the thin (20 nm) layer of amorphous carbon deposited on a copper substrate can be converted into graphene sheet as a result of annealing at a temperature of 1035 °C for 30 min in a flow of H_2 with the flow rate of 2 cm^3 min^{-1}. This process does not occur without hydrogen. The authors of Ref. [40] assumed the participation of hydrogen in reactions with the formation of gaseous hydrocarbons and a monolayer of graphene on the substrate.

4.2 Characteristic values of the methane concentration during graphene growth

It has been reported in Ref. [19] that, if for CVD growth at atmospheric pressure a methane concentration higher than 5 ppm (1 ppm = 10^{-6} g/g = 10^{-4}%) is used, then a multilayer graphite-like film will grow. Graphene is formed if the methane concentration falls down to a level of 41 ppt (1 ppt = 10^{-12} g/g = 10^{-10}%). In the case of a low-pressure CVD (LPCVD), a continuous film is obtained (as is shown in Ref. [13]), beginning from the flow rate of 8 cm^3 min^{-1} (cm^3 min^{-1} under standard conditions) under a gas pressure

of 1 Torr at a growth temperature of 1000 °C, and from 30 cm^3 min^{-1} at 900 °C. At a methane concentration equal to 13 cm^3 min^{-1} and the same gas pressure and growth temperature of 1000 °C, nucleation of the second layer occurs. As shown above, to decrease the concentration of growth nuclei and to enlarge the coarse graphene domains, flow rates of methane ranging 0.5–2 cm^3 min^{-1} are used [22, 25]. On the whole, the growth process depends on a large number of interdependent parameters, which makes it possible to only roughly outline some typical values of the concentration of methane necessary for graphene growth.

4.3 Methanol concentration during graphene growth

Let us consider, once again, the role of parameters such as the purity and the orientation of the copper substrate. In Ref. [41], the authors carried out a comparison of the dimensions of the growing domains and their quality for copper substrates with a purity of 99.9995% (HPCu) and 99.98% (LPCu). It was shown that an increase in the purity of the copper substrates makes it possible to obtain larger graphene domains of a more regular shape, apparently due to a reduction in the concentration of the nucleation centers. It has also been shown that the orientation of the crystallites composing the substrate influences the shape of the graphite domains (as is known, the structure of the Cu(111) plane is close to that of graphene).

An interesting approach was suggested in Ref. [42], where the growth was performed on one and the same substrate twice. First, few-layer graphene was grown; then, using lithography technique, periodically located square islands with a size of 500 nm were prepared, with the distance between them equal to 16 μm (Fig. 6). The second step of graphene growth on this foil with the nuclei formed in the above way led to the formation of graphene domains at each nucleus. As a result, ordered arrays of single-crystal islands of graphene with a size of more than 10 μm were obtained [43]. The measurements of the mobility of charge carriers gave values of approximately 10,000 cm^2 V^{-1} s^{-1}, whereas the mobility was less than 1000 cm^2 V^{-1} s^{-1} in the case of growth without nuclei, using the same regime. It has also been revealed that it is the islands of applied carbon-containing materials or hydrocarbonates that can serve as such nuclei [43].

The grown graphene can be removed from the surface making use of an electrochemical delamination from the copper substrate [44]. As a result, the copper substrate can be utilized repeatedly. It is interesting that the reuse of the substrate leads to a higher quality of the obtained layers, most likely because of the larger duration of the total annealing accomplished in the preparation of the substrate plate, which, as is known, improves the morphology of the surface. As a consequence, the sizes of the graphene domains grow. The resistivity of graphene layers upon repeated growth decreases from 2500 Ω/sq after the first cycle to 1600 Ω/sq after the third cycle. Simultaneously, the mobility of charge carriers increases almost twofold (from 2000 to 4000 cm^2 V^{-1} s^{-1}) [44]. This shows once again the importance of an appropriate surface preparation of the copper substrate for obtaining high-quality graphene.

5. Conclusions

The basic trend in the development of technologies for growing graphene by CVD methods is, at present, the search for methods of obtaining graphene sheets with large single-crystal domains. The record sizes of graphene domains are about 300 μm. It has been shown that the mobility of charge carriers in such domains (to $\sim$ 25,000 cm^2 V^{-1} s^{-1} on an SiO_2/Si substrate) exceeds by approximately an order of magnitude the mobility of carriers in a polycrystalline film. The possibility of attaining a regular arrangement of domains with the use of few-layer graphene nuclei is a second important and interesting achievement in the recent development of the technology of growing graphene. Note that, in contrast to lateral growth with the use of Ni pads, where the mobility of carriers is extremely low, growth with the employment of few-layer graphene nuclei demonstrates a high mobility of carriers ($\sim$ 10,000 cm^2 V^{-1} s^{-1}). A problem thus far is the necessity of provision of a hexagonal shape of the nuclei with an identical orientation in order to ensure their efficient joining and the possibility of obtaining a continuous film without a second (rapid) stage of growth. This possibility can, in principle, be ensured through growth on molten copper but is so far an unsolved problem at growth temperatures lower than the melting point of copper. It is also necessary to note the development of approaches that do not require the transfer of the grown film to a dielectric substrate. These approaches are very promising, since the transfer of graphene is a sufficiently complex technological operation, which sometimes critically determines the final characteristics of the obtained graphene sheet. However, the high level of the parameters of films obtained by this method has not been reached so far.

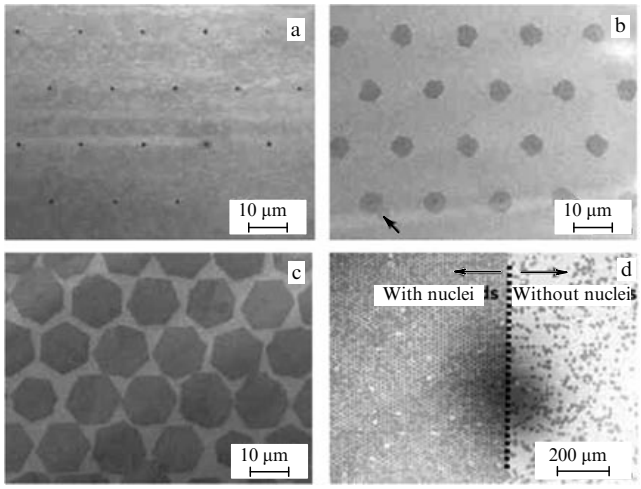

Figure 6. SEM images: (a) islands of nuclei formed from a few-layer graphene film using lithography technique (500 nm in size); (b, c) growth of graphene for (b) 5 and (c) 15 min at a temperature of 1050 °C, and (d) two regions of growth with nuclei and without nuclei [42].

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