

METHODS OF OBTAINING GRAPHENE

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Abstract: Graphene was first obtained at the beginning of the 21st century, and since then various methods have been developed for its synthesis. This variety is explained by the natural layered structure of graphite. A large number of methods is based on the idea of separating graphite layers. They are considered relatively cheap, productive and available in almost all laboratories.

Another group of graphene synthesis methods is based on the concept of creating graphene sheets from individual carbon atoms. These methods are technologically more complex and require appropriate specialized equipment.

Due to the wide range of graphene synthesis methods and their availability, researchers from all over the world can conduct experiments with this unique material in various scientific fields. This makes graphene an extremely promising object for further scientific research.

Key words: graphene, synthesis, intercalation, exfoliation, deposition, CVD, "top-down", "bottom-up" processes.

1. Introduction

After the discovery of a new allotropic form of graphite in the form of monolayers (graphene) in 2004 [1], this material began to be actively investigated, and various methods were developed for its production.

Today, there is a large number of methods of manufacturing this material. They exist due to the fact, that the natural material – graphite – has a layered structure, and individual layers of this material are graphene sheets. Therefore, most methods are based on the idea of separating the graphite into single layers using different approaches.

The choice of manufacturing method depends on several factors, such as the size, quantity, quality and price of the final product. The synthesis technique determines the structure and properties of the obtained graphene. There are different thickness variations of graphene, such as single-layer, double-layer, and multi-layer, and they have different applications in various fields of science and technology, such as energy storage, biotechnology, memory, electronics, sensors, etc. Researchers use different methods, especially when a large amount of material is required [2-3]. All methods of obtaining graphene are divided into two large groups, namely, obtaining graphene from the top down and from the bottom up [4-6].

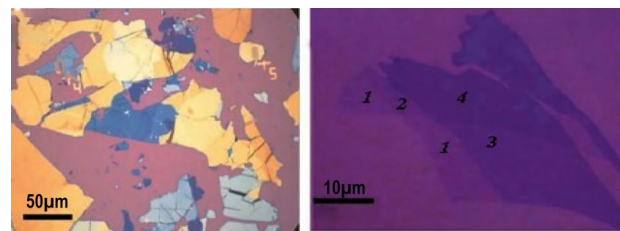
2. Processes "from top to bottom"

In the downward process, graphene sheets are obtained by exfoliation or separation of highly ordered pyrolytic graphite [4-6].

2.1 Mechanical peeling

A mechanical or micromechanical exfoliation method was a turning point in the history of graphene, and to this day, it is the key method for the synthesis of high-quality graphene for research purposes. Due to this method, it is possible to obtain high-quality samples with a size of 5 to 10 μm [5]. However, the non-uniformity of the thickness of the films obtained by this method and the high cost of production due to the low yield make this method unsuitable for mass production. These methods are a clear example of a bottom-up approach, when graphene precursors consist of graphite, which is disassembled layer by layer, forming graphene sheets [5].

A group from the University of Manchester, which includes two Nobel laureates, Geim and Novoselov, obtained graphene by micromechanically cleaving graphite using adhesive tape, which allowed them to divide the graphite into thin layers [1].



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Fig. 1 a) Optical photograph of several graphene layers.
b) Graphene layer of different thickness on a SiO_2/Si substrate [6]

These researches [1] used adhesive tape to obtain a single layer of graphene by exfoliation from highly ordered pyrolytic graphite (HOPG) with a thickness of 1 mm. For this, dry etched graphite (in oxygen plasma) was pressed against a layer of wet photoresist 1 mm thick on a glass substrate and baked. Baking was performed to attach the HOPG to the photoresist layer, and the exfoliation of the graphite flakes was achieved using an adhesive tape. Graphite flakes dispersed in acetone

were transferred to a cleaned SiO₂/Si substrate. Fig. 1(a) shows an optical micrograph of multilayer graphene flakes obtained by mechanical exfoliation on a SiO₂/Si substrate, and Fig. 1(b) demonstrates individual graphene flakes with different number of layers [6].

2.2 Chemical peeling

Various chemicals can be introduced between the graphite layers to produce graphite intercalation compounds. Intercalants increase the distance between the graphite layers. This also affects the characteristics of graphene, as increasing the distance between the layers affects the electronic connection between them. A different interlayer distance can lead to the fact that the material will have a different set of properties [5, 7].

Alkali metals can easily form intercalation compounds with graphite due to the difference in ionization potential between graphite and alkali metals. Viculis and his co-authors [8] used a chemical exfoliation method applying potassium as an alkali metal to obtain graphene nanoplates. The intercalated compound of potassium graphite KC8 was formed by the reaction of potassium with graphite at 200°C in inert atmosphere. During the dispersion of intercalated graphite in aqueous ethanol (CH₃CH₂OH), an exothermic reaction occurs, leading to the formation of graphene layers. Potassium ions dissolve in the ethanol solution, forming potassium ethoxide (KOEt) and producing gaseous hydrogen, which helps to separate the graphene layers [8]. However, care must be taken during this reaction because alkali metals, including potassium, react violently with water and alcohol. Therefore, an ice bath is used to control the temperature during the reaction. The main advantage of alkali metals, potassium in particular, is their small atomic radius, which allows them to easily penetrate into the interlayer space of graphite, as shown in Fig. 2.

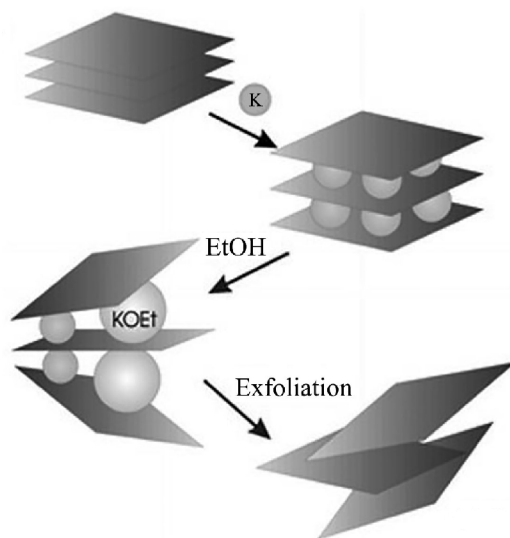


Fig. 2. Scheme showing the intercalation of potassium between layers in the process of chemical exfoliation [8].

Fig. 3 shows scanning electron microscope (SEM) images of chemically exfoliated graphene nanoplates. They are about 10 nm thick and consist of about 30 layers.

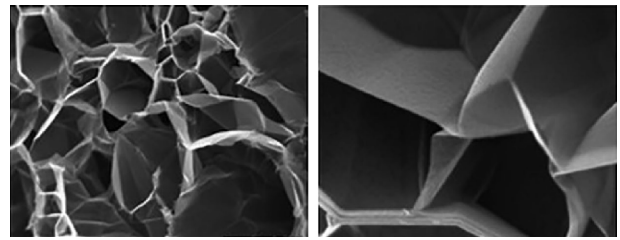


Fig. 3. SEM microphotographs of chemically exfoliated graphite layers [8].

The synthesis of graphene by chemical exfoliation is important and unique because it allows obtaining large amounts of graphene at low temperatures. In addition, this method is scalable [6].

2.3 Electrochemical peeling

Parvez and colleagues [9] reported an interesting method for exfoliating graphene from graphite using an electrochemical approach. They used a 0.1 M H₂SO₄ solution as an electrolyte, a graphite plate as an anode, and platinum darts as a cathode. The system was subjected to a current of 10 V, and the graphite flakes began to dissolve in the solution. After 2 minutes, researches began to separate the exfoliated graphite material using vacuum filtration. Then the sample was repeatedly washed with water to ensure removal of acid residues [9].

Lu et al [10] proposed a one-pot method for the synthesis of various forms of carbon nanoparticles, including graphene, by graphite exfoliation in ionic liquids. They conducted experiments dissolving 1-butyl-3-methylimidazolium tetrafluoroborate (1-hexyl-3-methylimidazolium hexafluorophosphate, or HMIH) in water used as an electrolyte for the electrochemical exfoliation of graphite. A static potential of 1.5 to 15 V was applied. The exfoliated particles were washed with water and ethanol to reach a neutral pH level [5].

2.4 Ultrasonic treatment

High-quality non-oxidized graphene layers can be obtained using ultrasound [5,11]. This method is an excellent example of a bottom-up approach to graphene synthesis, as it uses ultrasonic energy to separate layers of graphite. However, this method requires a significant amount of energy, since sonication is the only source of energy, which can cause scaling problems [12]. Fig. 4 shows the physical and mechanical exfoliation of graphite flakes under the influence of ultrasound [13]. Graphene obtained by this method can be used in the field of polymer fillers, transparent electrodes, and sensors [14].

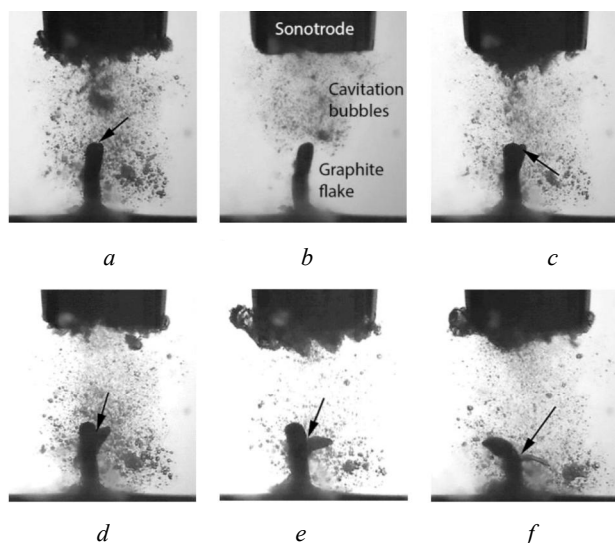


Fig. 4. A high-speed sequence (from a to f) of frames illustrating the physical and mechanical exfoliation of a graphite flake by a 3-mm ultrasonic source of 24 kHz. Arrows show the site of a split (exfoliation) with cavitation bubbles penetrating the split. 100,000 frames per second [13].

Tyurnina et al. investigated the effect of different ultrasound frequencies and physical dimensions of the sonotrode on the yield and properties of graphene [13]. The paper compared graphene obtained using sonotrodes with a diameter of 3 mm and 20 mm; graphene obtained with a 20 mm diameter sonotrode was of better quality and had fewer defects. This may be due to the fact that the sonotrode with a diameter of 3 mm created a concentrated cavitation zone with a fairly high acoustic intensity, which was destructive to the graphite flakes. Probably, the fractions of graphite powder at such a high intensity were destroyed faster being perpendicular to the graphite plane than separated due to the splitting of graphite layers [13].

Also, with the use of a larger sonotrode, it was possible to obtain thinner graphene samples and larger sizes up to $3 \mu\text{m}^2$. The quality of graphene was also studied depending on the frequency of ultrasound, where the frequency range varied from 20 kHz to 1174 kHz. The results of the study showed that a higher frequency separates the graphene layers better; at the output, graphene samples with a smaller number of layers and a larger area were obtained [13].

Solvent sonication is a modification of the sonication method and an obvious step forward. When solvents are used, graphene tends to re-connect after sonication due to the van der Waals forces. To avoid such problems, surfactants or dispersing agents can be added to the solution before sonication, thereby preventing the graphene sheets from rejoining. This method can be used to obtain graphene sheets from graphite without chemical modification. It also has a high final product yield of up

to 5.33 mg/mL due to the use of an ionic liquid (HMIH) and remains stable and environmentally friendly [15].

2.5 Pyrolysis method

Pyrolysis is a fairly simple and scalable process. However, the yield is low, and impurities are present in the final product [5]. This is a solvothermal synthesis of graphene with the use of a solvent interacting with the precursor [15]. This reaction is carried out in a closed vessel under high pressure with a 1:1 molar ratio of ethanol and sodium [6].

Sodium (2 g) and ethanol (5 ml) in a ratio of 1:1 are heated in a closed reactor at 220 °C for 72 hours to obtain a precursor of graphene - a solid solvothermal product. Then it is quickly pyrolyzed, and the remaining product is washed with deionized water (100 ml). The suspended solid is then vacuum filtered and dried in a vacuum oven at 100 °C for 24 hours. This method of solvothermal reaction can provide a graphene yield of about 0.1 g per 1 ml of ethanol, usually the yield is 0.5 g per reaction [5,16].

It was established that the obtained graphene layers have dimensions up to $10 \mu\text{m}^2$ [6]. The Raman spectra showed a broad D-band (defective) and G-band with an intensity ratio of -1.16 (IG / ID), which is characteristic of single-layer defective graphene. Although this process was cheaper, simpler and required low temperatures, the presence of a large number of defects reduced the quality of the graphene. This method of obtaining graphene has not become widespread [6].

2.6 Unpacking of carbon nanotubes

One of the options for making graphene is a method that uses carbon nanotubes (CNTs) as a starting material. This method is widely known as "CNT unpacking" [3].

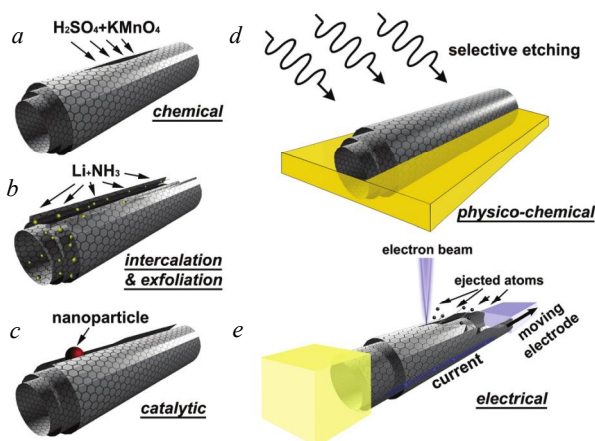


Fig. 5 Different methods of unpacking nanotubes [17].

Several methods of unpacking CNTs were developed. [5, 17]. Wet chemical methods (Fig. 5a), which include acid reactions, begin to break carbon-carbon

bonds with the help of H_2SO_4 and KMnO_4 [18]. Physicochemical methods (Fig. 5b) provide embedding carbon nanotubes into a polymer matrix followed by Ar plasma treatment [19]. The intercalation-exfoliation method (Fig. 5c) which consists in removing the tube caps by acid treatments, followed by treatment in liquid NH_3 and Li, and a further heat treatment [20]. The catalytic approach (Fig. 5d) being used, metal nanoparticles cut the nanotube in the longitudinal direction [17]. The electrical method shown in Fig. 5e provides unpacking the CNTs by passing an electric current through the nanotube [17].

2.7 Reduction of graphene oxide

With the help of chemical reduction of graphene oxide, it is possible to obtain graphene of various sizes, from several nanometers to several micrometers. Graphene obtained by this method can be used to make conductive inks and paints, polymer fillers, battery electrodes, supercapacitors, sensors, and many other devices [5].

Chemical reduction of graphene oxide is one of the traditional methods for obtaining graphene in large quantities. Three methods exist for the synthesis of graphene oxide: the Brody method [21], the Staudenmeier method and the Hammers method [6]. All of them are based on the oxidation of graphite with strong acids and oxidizing agents such as concentrated sulfuric acid, nitric acid, and potassium permanganate. The degree of oxidation may vary with the stoichiometric conditions of the reaction (pressure, temperature, etc.). Works by Brody et al. [21] first demonstrated the synthesis of graphene oxide by adding potassium chlorate (KClO_3) to a graphite suspension in the presence of the fuming nitric acid (HNO_3). However, this process was time-consuming, it involved several stages and was dangerous. In 1898, Staudenmayer and others modified the process by adding concentrated H_2SO_4 , which made it possible to obtain highly oxidized graphene oxide in a one-step process. Hammers and colleagues developed a popular method currently in use, where graphite is oxidized by mixing a graphite suspension in sodium nitrite (NaNO_2) and concentrated potassium permanganate (KMnO_4) without using HNO_3 [6].

Fig. 6 shows a schematic diagram of the synthesis of graphene oxide from graphite, using three aforementioned methods. When graphite turns into graphene oxide, the interlayer distance increases by two to three times, depending on the oxidation time. In the case of pure graphite, the interlayer distance increases from approximately 3.34 \AA to 5.62 \AA after one hour of oxidation. After prolonged oxidation for 24 hours, the distance increased to approximately 7.35 \AA [21]. During ultrasonic treatment in the solution of dimethylformamide

(DMF) and water with the DMF/water ratio of 9:1, the distance between GO layers is further expanded, forming individual layer suspensions. When hydrazine is treated with GO hydrate, it is reduced to graphene. The chemical reduction process is carried out using dimethylhydrazine or hydrazine in the presence of a surface-active substance or polymer to obtain homogeneous colloidal suspensions of graphene [6].

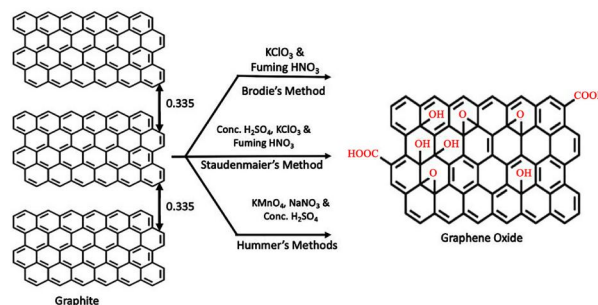


Fig. 6. Synthesis of graphene oxide [6]

The reduction of graphene oxide was carried out using sodium borohydride (NaBH_4), hydroxylamine, hydroquinone, ascorbic acid, etc. as reducing agents.

The chemical reduction method is the most useful one, since it removes most of the functional groups present in the graphene oxide intermediate, while the graphene surface structure is restored after the reduction reaction. However, the resulting graphene contains some defects due to the presence of residual oxygen functional groups (such as $-\text{OH}$ and $-\text{COOH}$), which causes some disorder in the electronic structure of graphene. This leads to a decrease in the electrical conductivity of the produced graphene compared to the defect-free graphene [6].

3. Bottom-up processes

In the ascending process, graphene layers are produced by increasing the nanosized material using the atomic or molecular arrangement of carbon [4-6].

3.1 Dry ice method

One of the ascending methods is the dry ice method. Graphene can be obtained by burning 3 g of Mg ribbon in a bowl of dry ice covered with another plate of dry ice (solid CO_2). The Mg must be completely burned in CO_2 and the residue stirred overnight in 100 mL of 1 M HCl . Mg and MgO dissolve in water. Then the mixture is filtered, and the residue is washed with deionized water to a neutral pH level. To redistribute the content of the residue, it is necessary to dry it overnight in a vacuum at $100 \text{ }^\circ\text{C}$, which gives a graphene yield of 680 mg (92 %) [5, 22].

3.2 Chemical vapor deposition (CVD)

The process of thermal chemical deposition from the gas phase involves the impact on the substrate of thermally decomposed precursors in a gaseous state, which

leads to the deposition of the product on the surface of the substrate at a high temperature. In many cases, deposition at high temperature is undesirable, so plasma reaction and deposition are used to lower the temperature. Depending on the quality, type of precursor, thickness of the deposited product, and structure, several types of CVD processes can be used, including thermal, plasma (PECVD), reactive, hot wall, cold wall, etc. [6].

Thermal CVD and PECVD are the most commonly used types of chemical vapor deposition to produce graphene. Fig. 7 [23] shows the diagram of the process of thermal CVD and plasma CVD is illustrated in Fig. 8 [24].

Thermochemical deposition of graphene from the gas phase involves feeding precursor gases such as methane, hydrogen, and argon in specific ratios into a quartz tube containing a substrate, such as copper, at high temperatures in a furnace (Fig. 7). Graphene is deposited over time, consisting of a monolayer, bilayer, or multilayer depending on given conditions, such as gas flow rate, reaction time, pressure, and temperature. The deposition of the high-quality graphene by the CVD method is usually carried out on substrates of various transition metals (their surface acts as a catalyst), such as Ni, Pd, Ru, Ir, and Cu, using various hydrocarbons, such as methane, benzene, acetylene, and ethylene [6]. Under the influence of a transition metal on a hydrocarbon gas at a high temperature, the substrate is saturated with carbon, and upon cooling, a thin film of carbon is formed [6].

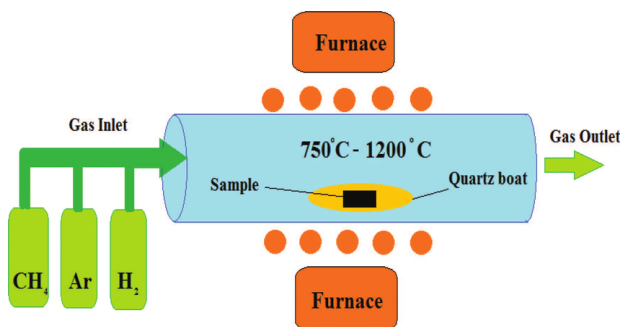


Fig. 7. Scheme of thermal CVD [23].

After growing graphene on metal substrates, the resulting graphene is transferred to another surface using copy etching, which allows for several chemically intact layers of graphene to be obtained. This is confirmed by Raman spectroscopy and HRTEM data [25].

Graphene growth by the CVD method was mainly carried out on Cu and Ni substrates. The problem of obtaining graphene on a nickel substrate was a long non-self-limiting growth, as well as the formation of a large number of folds. Copper substrates demonstrated a more favorable growth of graphene by the CVD method [25].

The graphene production process using plasma chemical deposition from the gas phase (Fig. 8) involves chemical reactions of reactive gases in a vacuum chamber in the presence of plasma, resulting in the deposition of a thin film on the surface of the substrate. Hence the name of the process is “plasma-enhanced chemical vapor deposition” (PECVD). Plasma sources in PECVD can be radio frequency microwave ovens and mutual induction (electric currents created by electromagnetic induction). The PECVD graphene synthesis process is performed at a relatively low temperature and shorter deposition time than other CVD methods, and is therefore more appropriate for large-scale industrial applications.

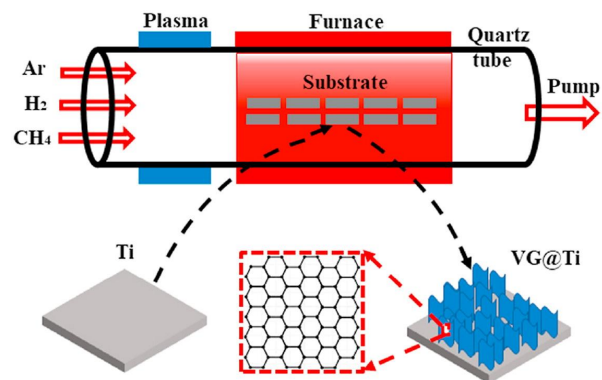


Fig. 8. Scheme of plasma CVD (PECVD) [24].

By controlling process parameters, it is possible to achieve catalytic-free growth [26]. RF plasma-enhanced chemical vapor deposition has been achieved using substrates such as Ti, SiO₂, Si, Al₂O₃, Mo, Hf, Zr, Nb, Cr, W, Ta, and stainless steel [29]. This method reduces energy consumption and prevents the formation of unwanted products or amorphous carbon [28].

3.2.1 Growth of graphene on Ni

The growth of graphene on nickel substrates is one of the earliest examples of graphene CVD and, as a result, one of the most intensively investigated. However, this system is also one of the most complex, and only recently the fundamental understanding of the growth and stability of graphite films on nickel has been reached [30].

Ni has the highest C solubility among the transition metals, absorbing about one percent of C atoms at high temperatures. In addition, the Ni (111) surface has the crystal lattice closest to that of the graphene among all growth surfaces of transition metals. Unlike other highly soluble metals (for example, Pt), Ni strongly interacts with the graphene layer, which leads to a significant modification of the electronic structure of graphene and alignment of epitaxial films by rotation. Although the formation of carbides is characteristic of many metals, Ni has a unique feature: the carbide phase, as a rule, is

stable only up to relatively low temperatures (460° C), while graphene on Ni is stable up to 650° C. Above 650° C, graphene dissolves in nickel [29, 30].

The first evidence of obtaining large-scale monolayer graphene by the CVD growth method was recorded by Obraztsov et al. [31] in 2007. Growth was achieved using methane and hydrogen precursors in a direct current discharge at approximately 0.5 A/cm². The structure of deposited graphene shown in Fig. 9 exhibits anomalous surface ridges that can be described as graphene fold lines. The formation of ridges in graphene occurs due to the difference in the coefficients of thermal expansion of graphene and nickel. Raman spectroscopy and scanning tunneling microscopy (STM) confirmed the presence of several layers of graphene with a thickness of approximately 1-2 nm [31].

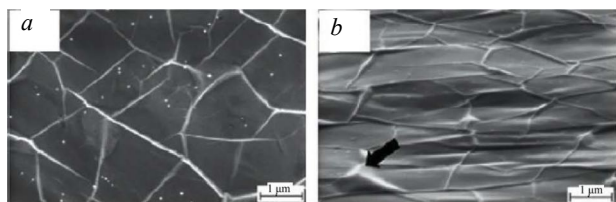


Fig. 9 SEM image of synthesized graphene on Ni(111) by the CVD method using a constant discharge [30].

3.2.2 Growth of graphene on Cu

Nowadays, copper is most often used as the main substrate to obtain large-area graphene films. Copper foil is a cheap material, and graphene can be grown on it in standard quartz tube furnaces. This technology has become very popular due to the convenience and availability of growing graphene films [29].

To obtain single-layer graphene films of arbitrary size that can be transferred to a substrate, Li et al. developed a CVD process in which predominantly single-layer graphene films can be grown [25]. In their study, a copper foil substrate was heated to 1000°C in a quartz tube furnace in a gas mixture containing both CH₄ and hydrogen. After 10 minutes of growth, the authors found that the copper foil was completely covered with graphene. A polymer-assisted transfer process was used, at which graphene was deposited on a polymer substrate and then copper foil was dissolved. After that, the polymer material was washed off with acetone, leaving open single-layer graphene [30].

As it was discovered later, the growth of graphene on Cu substrates is self-limited at the level of one layer [24]. Since the catalytic activity of the copper substrate is the primary mechanism for the decomposition of the hydrocarbon precursor gas (usually CH₄), once the graphene film becomes large enough to cover the entire surface of the copper, there are no more exposed copper atoms left to catalyze the decomposition reaction. Since

the growth temperatures of graphene are insufficient for the thermal decomposition of CH₄ (i.e., without the presence of an active catalyst), as soon as the graphene film covers the entire surface, the growth stops. It has also been shown that when a graphene island is in contact with a step on a copper surface, graphene continuously grows over the surface structure [32].

Despite the overwhelming evidence that graphene films grown by CVD on metal foils are polycrystalline, this growth method has been widely adopted and is routinely used due to the relative ease with which monolayer films can be grown. Most copper films are produced by cold rolling, which, due to plastic deformation, leads to a surface with a (100) plane [31].

4. Conclusions.

During the almost twenty-year history of research and application of graphene in various fields of science and technology, many methods for its production have been developed. Graphene can undoubtedly be considered the material with the largest number of synthesis methods. This fact is the key to the popularity of this material.

To date, there is no universal method for the synthesis of graphene, and this is not a problem at all. Researchers can choose the method according to their needs and capabilities. For example, simple and affordable methods of grinding graphite can be used to use graphene as a component in lubricants or inks. In the case when shape and size are not of great importance, but graphene is needed for biological or chemical research, chemical, mechanical or ultrasonic separation methods can be used.

However, if high-quality graphene with consistent thickness and precise dimensions is to be obtained for the use in micro- and nanoelectronics, advanced bottom-up synthesis methods are best suited for such tasks.

For future tasks related to the use of graphene in nanoelectronics, it is important to develop new methods and improve existing ones in such a way that they would be scalable, efficient and affordable from a financial point of view. This will help graphene devices compete with traditional semiconductor devices in the future.

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МЕТОД ОТРИМАННЯ ГРАФЕНУ

Роман Біляк

Графен був вперше отриманий на початку 21-го століття, і з того часу було розроблено різноманітні методи для його синтезу. Ця різноманітність пояснюється природньою шаровою структурою графіту. Велика кількість методів ґрунтується на ідеї розділення шарів графіту. Вони вважаються відносно дешевими, продуктивними та доступними практично в усіх лабораторіях.

Інша група методів синтезу графену базується на концепції створення графенових листків з окремих атомів вуглецю. Ці методи є технологічно складнішими і вимагають відповідного спеціалізованого обладнання.

Завдяки широкому спектру методів синтезу графену та їх доступності, дослідники з усього світу можуть проводити експерименти з цим унікальним матеріалом у різних

наукових галузях. Це робить графен надзвичайно перспективним об'єктом для подальших наукових досліджень.



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