https://doi.org/10.15407/ufm.23.02.268

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PROSPECTS OF APPLICATION AND GLOBAL SIGNIFICANCE OF GRAPHENE

The review article is an excursus into the world publications describing the properties of graphene, methods of synthesis of it and variety of its application fields. The paper describes in detail the structure of graphene as well as the methods for its fabrication: micromechanical cleavage, chemical stratification, epitaxial growth, and chemical gas-phase deposition, including their advantages and disadvantages. In addition, the review contains information on the electronic, mechanical, optical, and chemical properties of graphene, which lend its uniqueness. Due to its unique properties, graphene and its modified quasi-two-dimensional structures are the objects of increased scientific interest in various fields of science, such as energy, electronics, optoelectronics, medicine, bioengineering, aerospace, aviation, ecology, materials engineering, *etc.* In order to expand the journal readership among the physicists, chemists, and materials scientists, who are not deep specialists in graphene science, the style of the present review is somewhere close to popular science one.

Keywords: allotropic forms of carbon, graphene, graphene films, nanomaterials, micromechanical cleavage, chemical stratification, epitaxial growth, chemical gas-phase deposition, bioengineering, optoelectronics.

1. Introduction

Nanotechnology and nanomaterials belong to new field of science and technology, which, overlapping with various disciplines, explores nanoworld. Materials' structure and particles at the level of 1-100 nm have completely different properties and behaviour [1]. Chemists who

Citation: A.I. Denissova, A.V. Volokitin, and I.E. Volokitina, Prospects of Application and Global Significance of Graphene, *Progress in Physics of Metals*, 23, No. 2: 268–295 (2022) have managed to synthesize hundreds of thousands of different substances, materials and structures have made the main contribution to the obtaining and study of nanomaterials. They have discovered and studied the properties of periodic table's each element, one of which is carbon. Being a unique component of great number of both organic and inorganic compounds, carbon has the following allotropic forms: graphite, diamond, nanotube, fullerene and many others (Fig. 1) [2]. The oneatom-thick form of graphite with two-dimensional properties forms graphene, which, due to its amazing properties, carries the title of 'miracle material' [3].

2. Material and Its Production Techniques

The graphene (Fig. 1, left) has a hexagonal cellular lattice in the form of bonded sp^2 atoms plane with a molecular bond of 0.142 nm length [2]. Separate layers of graphene in graphite with interplanar spacing of 0.335 nanometres are held together by Van der Waals forces, which can be overcome in the process of graphene from graphite peeling [3].

Research on graphene based on theoretical descriptions of its composition, structure and properties has expanded rapidly since this substance was first discovered in 2004 by two scientists from the British University of Manchester, Konstantin Novoselov and Andrey Geim, who were awarded the Nobel Prize in Physics in 2010 'for pioneering experiments on the two-dimensional material graphene'. In order to obtain graphene, the scientists used applied to the adhesive tape piece of graphite, which was cut in half, many times being glued and unglued to the adhesive tape. They carried out these actions in order to obtain the ultimate result, *i.e.*, one last transparent layer, namely, *graphene*. Then, obtained material was transferred to the substrate, which was called the method of 'exfoliation' or 'chipping' [4].



Fig. 1. Carbon structures: graphene, carbon nanotube, fullerene, diamond, and graphite [2]



Fig. 2. Scheme of graphene obtaining through the micromechanical chipping [6]

The main graphene obtaining methods include micromechanical detachment (exfoliation), chemical delamination, epitaxial growth and chemical gas-phase deposition [5]. The first and simplest method of graphene production was the *micromechanical exfoliation* described above, which involves the separation of a thin film with the thickness of several hundred layers from a plate of bulk pyrolytic graphite using an adhesive tape (Fig. 2) [4, 6].

The single-layer graphene film was subsequently transferred to an oxidized silicon substrate, where it was held by Van der Waals forces. Significant advantage of this method is the production of the highest quality graphene, which makes it suitable for use in electrical devices, such as a quantum transistor. The disadvantages of this method include the lack of large-scale production possibility, since this method is considered manual [3].

In order to obtain large area graphene, more expensive and complicated process, namely, chemical vapour deposition is used. In mixtures consisting of carbon-containing gas, argon and hydrogen in the process of heating under different pressures at temperatures below 400 °C, the process of substance into carbon and components decomposition is carried out. Carbon atoms are deposited on a nickel substrate up with the temperature of 650 °C. During the increasing of temperature up to 800 °C, the process of carbon atoms diffusion with the nickel substrate is started. When the maximum heating temperature of 950-1000 °C is reached, the heating process stops and the sample cools down to room temperature. This causes the nickel plate lattice shrink and pushing of carbon atoms to outward, which are combining into graphite structure. Compliance with certain synthesis parameters: thickness of nickel substrate, heating time and temperature, sample-cooling speed makes it possible to obtain a thin graphene film, as well as graphene monolayer. Since the solubility of carbon in copper is in 1000 times lower than in nickel, the diffusion process of the deposited carbon in copper does not occur. Growing of copper substrate temperature increases the possibility of larger area graphene film obtaining. This method makes it possible to obtain only one-layer graphene, because copper is a catalyst in the carbon deposition process [7]. However, there was a difficulty in graphene layers removing from the metal substrate without graphene damaging. Nevertheless, studies conducted in 2012 showed that by analysing of graphene interfacial adhesion energy, it is possible to effectively separate graphene from the metal board on which it was grown, and theore-

ISSN 1608-1021. Prog. Phys. Met., 2022, Vol. 23, No. 2



Fig. 3. Scheme of graphene film formation on the surface of a nickel or copper substrate by chemical deposition [8]

Fig. 4. Methods of obtaining graphene by splitting precursor materials [9]

tically use the board for future applications an infinite number of times. In addition, the quality of the graphene isolated by this method was high enough to create molecular electronic devices [3]. The scheme of graphene film formation on a nickel or copper plate is shown in Fig. 3 [8].

Another chemical method of graphene obtaining is *chemical cleavage*, which consists in obtaining of graphene in the process of graphite oxide recovery. In this method, special chemical oxidizers are used, acting on the layers inside the graphite, thereby, increasing the distance between the layers inside the crystal. It leads to interlayer interaction forces energy decreasing and promotes decomposition of the layers in the liquid phase (Fig. 4) [9]. The process of graphite liquid-phase separation also practiced using surface-active organic liquids, which entering into graphite causes increasing of distance between layers and, with the help of mechanical action after, make it possible to obtain graphene sheets. The material produced by this method contains not only single-layer, but also two- and multilayer samples of graphene, up to several micrometres [10].

Epitaxial method implies the growth of graphene on metal substrates of such single crystals as nickel, platinum, palladium, iridium, ruthenium, etc. due to the dependence of carbon solubility value in transition metals on the temperature above 1000 °C. Further, the solubility of carbon decreases because of decreasing temperature using high and ultrahigh vacuum with a pressure of 10^{-10} mbar. In this case, the process of crystal lattice compression takes place with the carbon coming to the surface and subsequent graphene formation (Fig. 5) [11]. The advantage of this method is that if the crystal is of good quality, the area of the synthesized graphene film is equal to the crystal surface. On the other hand, it is practically impossible to transfer the synthesized substance to the final substrate without damage [12].



Fig. 5. Diagram of the epitaxial growth process of graphene (E) [11]

Irish physicists have developed a method of creating graphene at home. To do this, 500 ml of water, 10-25 ml of any detergent, and 20-50 g of ground slate need the mixing. Then, just a kitchen blender of at least 400 W, working from 10 to 30 min, is used until the appearance of suspension from the graphene flakes. The resulting material will have a high

conductivity, which will allow using it in the electrodes of photocells. In addition, graphene fabricated in domestic conditions can improve the properties of plastic [13].

3. Properties of Graphene

The properties of any material are determined not only by the chemical composition, but also by atoms arrangement. Everyone knows how different diamond and graphite are, although, as well as graphene, are allotropic forms of the same carbon atoms. Recent years, the interest in graphene has been growing exponentially due to its wide range of unique properties [1]. One of the graphene peculiarities is that the bond between the carbon atoms forming the lattice is the strongest chemical bond in nature. Because of this, the graphene lattice is exceptionally regular; it is almost impossible to make any defects there, and mobility of its electrons is colossal [3]. For example, its sp^2 coupling and high symmetry provide exceptional transport properties. Electrons in graphene can move freely at very high speeds with negligible scattering due to the unique arrangement of carbon atoms in graphene. This saves energy that is usually lost in other conductors. Researchers have discovered that electrons in graphene are not slowed down or localized, so even under nominally zero carrier concentration conditions, graphene has the property of electrical conductivity [3]. So-called massless Dirac fermions, which have lost their mass or rest mass, are formed because of the interaction of electrons in carbon and periodic potential of cellular graphene lattice, which allows graphene to conduct electric current continuously [14].

One atom thick graphene is the thinnest and lightest compound known to people. For comparison, one square meter of graphene weighing approximately 0.77 mg has a strength limit of 130 GPa and Young's modulus of 1 TPa, which is 100–300 times higher than steel. A sheet of graphene with thickness of one atom can withstand the pressure of a pencil point, on the other side of which 'an elephant balances' [1]. In addition, graphene has the best thermal conductivity at room temperature from 3000 to 5000 W \cdot m⁻¹ \cdot K⁻¹ (for comparison, the thermal conductivity of Cu is circa 400 W \cdot m⁻¹ · K⁻¹). Graphene possesses the highest electrical conductivity: the charge carrier mobility is 1000 times higher than in Si, and can be more than 10⁶ cm² · V⁻¹ · s under certain conditions [15].

Another remarkable property of graphene, which belongs to the optical ones, is its uniform absorption of light in the visible and near-infrared parts of the spectrum, namely, optical transparency is of 97.7% [16]. Graphene is not only strong and transparent; it is also characterized by excellent flexibility, and a plate made of this material can be stretched by almost 20% [15].

The peculiarities of graphene chemical properties include the fact that, due to its two-dimensional structure, each individual atom participates in a chemical reaction from two sides. It is known that graphene has the highest ratio of sharp carbons (compared to similar materials, such as carbon nanotubes), and carbon atoms at the edge of graphene sheets have a special chemical reactivity [17]. In addition, recent research at the University of Manchester has confirmed the ability of graphene to 'self-repair'. When the crystal lattice of graphene film is damaged, graphene atoms attract free carbon atoms, filling the formed 'holes' as necessary [1].

For comparison, layered boron nitride has the same crystal structure as graphene, boron atoms replace only half of carbon atoms in it, and the other half is replaced by nitrogen. The properties of this material are quite different: if graphene is a semimetal with a very large electronic conductivity, then, boron nitride is a wide-gap insulator. It has approximately the same energy gap as diamond [3]. Another popular material now is molybdenum disulphide. Its parameters are already typically semiconductor, very close to what we have in ordinary three-dimensional silicon or germanium. It is also very important that two-dimensional materials can be combined (designed in layers): a layer of graphene, a layer of boron nitride, and then a layer of graphene again. Electrons will penetrate (tunnel) from graphene to graphene through boron nitride. These combinations do not exist in nature, but can be made artificially, with astonishingly interesting new physics and possibly new technical applications [18].

Currently, chemists, physicists, and electronic engineers have already become interested in the unique capabilities of graphene. After all, just a few grams of this substance can cover an area equal to a soccer field [4].

In addition, graphene allows creating a wide variety of composite materials with amazing properties. It sounds fantastic, but adding graphene to almost any material (metals, cement, ceramics, polymers, paints, coatings, glass, *etc.*) improves its properties of strength, durability and resistance to external influences. For example, adding less than 0.05% by weight of graphene to the concrete makes the concrete fine-grained, closes the pores, makes it almost watertight, its aging rate decreases, the strength properties increase significantly [19].



Fig. 6. Graphene oxide combined with diophilized carbon [21]

Researchers are actively studying the structure of graphene, which has attached oxygencontaining functional groups or (and) molecules inside or on the edges of carbon mesh. It is an oxide of the most solid nanosubstance, which is the first two-dimensional material that has reached the stage of commercial production. Scientists have made centimetre-long samples from nano- and microparticles of this structure. Recently, Chinese scientists obtained the graphene oxide combined with diophilized carbon. This is a very light material, a centimetre cube of which is held on the petals of a small flower. However, at the same time, the new

substance, which contains graphene oxide, is one of the hardest in the world (Fig. 6) [20, 21].

The race for leadership in the production of graphene and materials with its admixtures began in the world. Annual sales growth of graphene components and products based on it today is about 37% per year. However, the world market of graphene is still very small, estimated at 150 million dollars. Nevertheless, by 2030, the volume of sales of products based on graphene could reach 800 billion dollars, and the world is at the start of the graphene wave. Developments based on graphene enjoy state support in many developed countries. In the European Union, e.g., the project Graphene Flagship was launched; investments in 2014– 2020 are estimated at 1 billion euros. In the history of EU science support, one can hardly find another project as large as this, aimed at putting into practice of relatively recent scientific discovery. Among the leading countries actively working with graphene, in addition to the USA and EU, there are Australia, Brazil, Israel, India, South Africa, and Japan. Undoubtedly that the undisputed leader in graphene research is China, which owns more than half of the world's publications and patent applications [22]. In 2013, China created the Graphene Industry Innovation Alliance, besides the country's leadership made the industry of new graphene-based materials one of the priorities of its 14th five-year plan (2021-2025) [7].

4. Applications of Graphene

4.1. Energy Industry

Global demand of energy, especially electricity, is steadily increasing. According to Energy Information Administration (EIA) USA statistics, the world electricity consumption in 2050 will be 79% higher as compared, e.g., to 2019 [23]. The highest growth is expected to occur in Asia, due to the constant growth of population and rising living standards in developing countries [22]. The intensive electrification of transportation is also an important reason for the increase in electricity needs around the world. These rapid challenges can only be solved by significant future technological breakthroughs in the production, transportation, and storage of electricity [24]. Intensive research in these areas also covers several applications of new materials. Perhaps, the most studied new material is graphene, the 'miracle material' of the XXI century. Because of rare combination of unique properties, graphene has the potential for application in many fields, such as energy (solar energy, batteries, and supercapacitors), electronics, optoelectronics, touch screen and display technology, lighting, sensors, biotechnology and composites, photodetectors with ultrawide bandwidth, etc. [25].

For the first time, the German mathematician Holger Thorsten Schubart, who proved more than 10 years ago that graphene can transform surrounding electromagnetic fields into the electric current, announced the possibility of electric power sources creating using graphene as a basic element. Based on his practical experience and the results of laboratory experiments, together with a group of scientists from German-American company Neutrino Energy Group, he invented the electrogenerating multilayer nanomaterial made of alternating layers of graphene and doped silicon, deposited on the metal foil from vapour phase. The total thickness of nanomaterial is of 1020 nm [26].

At the same time, graphene is widely studied by scientists from the Massachusetts Institute of Technology (MIT) in USA. However, their achievements are more modest compared to the results achieved by scientists of Neutrino Energy Group. The field of research is direct electric current. These high-frequency waves of radiation, known as 'T-rays', are produced by almost anything that radiates heat, including our own bodies and inanimate objects around us. Any device that sends out Wi-Fi signal also emits terahertz waves, electromagnetic waves with a frequency between microwaves and infrared light. 'We are surrounded by electromagnetic waves in the terahertz range' as Hiroki Isobe, a postdoc at the materials research laboratory of MIT, said. 'If we can convert this energy into an energy source that we can use for everyday life, it will help solve energy problems we face now', he added [27].

In the future, as MIT aimed at converting the energy of the surrounding terahertz waves, graphene has the potential to revolutionize the energy industry. Graphene makes it possible to generate energy in a completely new way. This material has ability to allow positively charged hydrogen atoms to pass through it is impermeable to other gases, including hydrogen itself. This opens incredible prospects for scientists to create fuel cells based on hydrogen. For instance, it will be possible to

collect hydrogen from the air in such cells and then using graphene to obtain electricity and water, producing almost no waste [28].

Physicists from the United States showed that graphene could be used for energy collecting; it can generate energy using environment. Scientists at the University of Arkansas have developed a circuit that can capture thermal motion of graphene and convert it into electric current. 'An energy-saving circuit based on graphene could be embedded in a chip to provide clean, limitless, low-voltage power for small devices or sensors' as Paul Thibadeau, who participated in experiment, said [29].

Simple acrylic paint, added with small portion of graphene, becomes conductive, which can already find many practical applications. When voltage of 18 V is connected to surface, the wall heats up, which, *e.g.*, can be used as an effective and cheap means against icing of roofs and storm drains [28].

A group of physicists from the University of Arkansas is developing in a slightly different direction. They propose to control the flow of electrons by changing of mechanical stress in the material. It has been observed that, if a mechanical force is applied to a graphene film, its electrical properties are changing as if the material were placed in a magnetic field. To use this property, it is necessary to learn how to control the mechanical stress. Researchers from the University of Arkansas conducted following experiment. They stretched graphene membranes over thin square frames and scanned graphene surface with tunnelling microscope-using direct current. The scanning tunnelling microscope uses a very small electric current to create surface topography map. To keep current constant while scanning surface topography, this type of microscope changes the voltage at the tip of tunnelling probe as it moves up and down. As observed, the shape of the membrane also changes as it bends and tends to move closer to the probe. The shape of the membrane changed depending on the charge between the probe and the membrane. By changing the voltage at the probe, it is possible to control the mechanical tension of the membrane. In a free state, graphene membranes have an irregular shape. This is an obstacle for their use in electronic devices, because membrane conductivity drops sharply at ruptures. For better understanding of this property, theoretical system containing graphene membranes was investigated. Scientists compared the magnitude of mechanical stress and determined location of microscope probe relative to the membrane. It turned out that interaction between membrane and probe depends on probe location. From these data, the pseudomagnetic field for a given voltage and mechanical force can be calculated. As a square frame confines the membrane, strength field is changing from positive to negative. In order to create a non-oscillating field, triangular cell has to be made. It may be possible to find a way to control pseudomagnetic properties of graphene (Fig. 7) [18, 30].

ISSN 1608-1021. Prog. Phys. Met., 2022, Vol. 23, No. 2

In Italy, scientists are developing solar cell based on graphene and organic crystals. This technology allows making solar cells larger, which increases the efficiency of energy collection and makes production cheaper by 4 times. Now, solar batteries are created based on semiconductor silicon, and they have fundamental efficiency limitations, they can 'catch' only a little more than half (58%) of solar spectrum, and most of solar energy is transferred into heat. The use of graphene film will not 'catch' most of the solar photons only, but also use



Fig. 7. Graphene membrane [30]

along with the semiconductor thermoelectric effect for solar energy conversion. Now, photovoltaics based on semiconductors has reached 22% efficiency (until recently it was 4%), but this is almost the limit, films based on organic semiconductors can add 1-2%, but the use of graphene will mean significant increase in efficiency [31].

According to the Science Daily editors, there is a development of a group of scientists from the Stevens Institute of Technology (USA), which proves that champignon mushroom can be transformed into electricity generating source. There is long known to science a special kind of bacteria called cyanobacteria, which can produce electricity without any aids. Their use for this purpose seems quite logical, but there is only one 'but'; cyanobacteria are very poorly adapted to artificial nutrient materials. Searching for the most suitable habitats for bacteria, scientists found that they could survive very well in the heads of champignon mushrooms. Besides, they live several times longer in the heads of live mushrooms. However, experts did not stop on it, they have created the first 'bionic hybrid mushroom'. Using 3D-printer, they put a net of graphene electro-conductive ink on the surface of mushroom head and covered it with clusters containing cyanobacteria. These two layers are printed in such a way as to have several points of intersection for signal transmission. The author of work, Manu Mannoor, says that, by combining the cyanobacteria, which can produce electricity, with nanoscale materials capable of collecting current, scientists have been able to access the unique properties of both, creating completely new functional bionic system. Printed branched net of graphene serves to collect electricity, while cyanobacteria produce it. Mushroom head acts as a substrate for bacteria to feed. Production of electric current starts, when they are exposed to light [32].

4.2. Electronics

The largest company manufacturing new nanomaterial is located in China. The name of this manufacturer is Ningbo Morsh Technology. It began producing graphene in 2012. The main consumer of this nanomaterial is Chongqing Morsh Technology Company. It uses graphene for production of conductive transparent layers, which are inserted into sensor displays [22].

Some experts believe that graphene can even provoke a new leap in development of human civilization. Scientists say that the silicon era will soon be over, because silicon element base modern technology is already coming to its technological and physical limit, and in this sense, graphene could be a good alternative. The use of graphene in electronics will help create faster and more powerful systems [20].

Since graphene is completely transparent, one of the most commercial applications of graphene will be optoelectronics [33], namely: liquid crystal displays, touch screens, organic LEDs. What is currently used in modern touchscreens, cell phones, etc., is made on basis of indium oxide. However, indium is a rare metal, expensive, and its deposits are few. Therefore, the producers of cell phones and other equipment have long been seriously interested in graphene as a possible material for touch screens. Especially intensive work on it is carried out in Korea and China; pioneer of this research was Samsung Company. Relatively recently, well-known Nokia company took out a patent for light-sensitive matrix. This important for optical devices that element contains several layers of graphene. This material used in camera sensors significantly increases their sensitivity to light (up to 1000 times); at the same time, there is a decrease in power consumption. High quality camera for smartphone will also contain graphene. As for potential electronic applications, scientists are actively working on the development of such devices as electronic paper based on graphene with the ability to display interactive and updated information, as well as flexible electronic devices such as portable computers and TV's [34]. At the Mobile World Congress 2017, FlexEnable Company demonstrated graphenebased full-colour pixel matrix for energy-efficient displays and displays with electronic ink. These screens will have thickness of ordinary paper. In addition, these matrices will be flexible, which eliminates need for thick protective glass [35]. Currently, graphene paper is already actively used for chemical filters, protective layers, components of supercapacitors and electric batteries, various electronic and optoelectronic components, antibacterial medical bandages creation. New prospects are opening up for a wide range of applications from graphene paper (graphene ink, flexible biosensors) to biodegradable nanocomposites. Graphene electrodes are highly durable and more transparent than modern tin-indium



Fig. 8. (a) Simplified scheme of created resonator, where in the inset, SEM-microphotograph of the device. (b) The transmission spectrum for the open circuit (S_{21}) : amplitude (1) and phase (2). (c) Output power spectrum for the created graphene resonator [38]

analogues. In addition, this new technology is cheaper and more environmentally friendly, since it does not require usage of rare metals [36].

Although graphene was first obtained at the University of Manchester, research on this material is carried out all over the world, and the largest number of graphene usage patents belongs to China. It is not surprising that the largest electronics manufacturer in this country has become one of the first brands that introduced graphene in its products. Thus, Xiaomi Mi Pro HD are headphones with graphene diaphragm, which allows transmitting louder, cleaner and richer sound. Xiaomi also has PMA A10 therapeutic belt made of graphene-coated fabric [34].

The transition to all-carbon electronics will require not only transistors, resistors and capacitors, but also oscillators and resonators that convert direct current into periodic signal. Exactly, they are providing so-called 'clocking', or reference frequencies in circuits are responsible for timing in telecommunications. Accordingly, without this miniature device, it is impossible to imagine neither flash memory, nor cell phone, nor modern TV.

The most accurate resonators are based on plates cut out of monocrystalline quartz along the specific planes. If the accuracy is not so important, they are replaced with the piezoelectric resonators based on ceramics, such as PZT. However, to the dismay of all around the world engineers, this part is almost the main stumbling block on the way to reduce the size of electronic devices. This is where nano- and microelectromechanical devices (NEMS and MEMS) come to help, the ideology of which scientists from Columbia University, together with colleagues from Korea used in the development of graphene NEMS resonator. Nevertheless, not simple, this is also capable of tuning the operating frequency within 14% during applied voltage changing. In addition, as a confirmation of their invention practical significance, researchers assembled small FM radio transmitter, using described above gra-



Fig. 9. Change of resonator frequency [39]

phene oscillator, and then received and decoded the song signal (Figs. 8-10) [37-40].

The possibility of quantum computers practical use became one more step closer thanks to graphene. Specialists from the Massachusetts Institute of Technology and their colleagues from other scientific institutions were able to calculate superposition time with graphenebased qubits. Traditional computers store and process information in bits, working in the binary system of information measurement, and the data acquire the state of 'zeros'

or 'ones', which are understood by the computer in the form of certain commands. Qubits are used in quantum computers as elementary units of information, which can acquire simultaneous states of 'zeros' and 'ones'. Such peculiarity allows them to surpass considerably computational power of usual computers. Moreover, the longer qubits can remain in this state (also known as coherence time), the more productive quantum computer will be. Scientists did not know the coherence time of graphene-based qubits; so, in new study, they decided to calculate it and, at the same time, to see whether such qubits are able to be in superposition. According to the calculations, superposition time of graph-

ene qubits is 55 ns. After that, they return to their 'usual' state of 'zero'. In this study, scientists were motivated by the possibility of graphene properties using to improve the performance of superconducting gubits. Scientists showed for the first time that graphene-containing superconducting qubit can temporarily assume a quantum coherence state that is



Fig. 10. Signal of music composition [39]

Fig. 11. Flat area with forbidden zone for bilayer (BLG) and multilayer (MLG) graphene [43]

a key condition for building more complex quantum circuits [41]. Researchers led by Joel Yi-Yang Wang, for the first time, created device that allowed to measure coherence time of graphene qubit (primary qubit metric) and find out that the superposition time of these qubits has sufficient duration, allowing person



to control this state [34]. The 55 ns coherence time for a qubit may not seem like much. It is actually not much, especially considering that qubits based on other materials have shown coherence times hundreds of times longer than this, indirectly indicating that they have higher performance for quantum computers. However, graphene qubits have their own advantages over other types of qubits, researchers noted. For instance, graphene has one very strange, but useful feature; it is able to acquire properties of superconductivity, 'copying' it from neighbouring superconducting materials. Scientists from Massachusetts Institute of Technology [27] tested this property by placing a thin sheet of graphene between two layers of boron nitride. Placing graphene between these two layers of superconducting material showed that graphene qubits can switch between states when they are exposed to energy, not magnetic field, as it happens in qubits made of other materials. Advantage of this circuit is that a qubit in this case begins to act more like a traditional transistor, opening possibility of combining more qubits on a single chip. If we talk about qubits based on other materials, they work using magnetic field. In this case, current loop would have to be integrated into the chip, which in turn would take up extra space on chip and also interfere with nearby qubits, resulting in computational errors. Using graphene qubits is more efficient, as two outer layers of boron nitride act as a protective shell, protecting graphene from defects through which running along the chain electrons could leak. Both of these features can really help in practical quantum computers creating. The short coherence time of graphene qubits does not scare scientists at all. Researchers note that they can solve this problem by changing the structure of graphene qubit. In addition, specialists are going to understand in more detail how electrons move through these qubits. Using precise analysis of the band structure, scientists have identified an area not seen before. As A. Varikhalov stressed, though the double layer of

graphene has been studied earlier, because it is a semiconductor with a band gap, and the ARPES tool in BESSY II has a high enough resolution to see flat zone near band gap (Fig. 11) [42, 43].

This flat zone is a prerequisite for superconductivity, but only if it corresponds to the so-called Fermi energy. In the case of bilayer graphene, its energy level is only 200 meV below Fermi energy, but flat zone energy level can be increased to the Fermi energy by doping with foreign atoms or by applying an external voltage, so-called gate voltage [42].

Since the electrons' mobility in graphene is much higher than in silicon, digital cells made of graphene provide higher frequency of operation. Some companies have already claimed success in this area. For example, IBM transistors operate at a frequency of 26 GHz and are of about 240 nm in size. Since there is an inverse relationship between size of transistor and its performance, increasing of operating frequency is achieved by reducing its size [44].

Researchers from the University of California in Los Angeles and California NanoSystems Institute have demonstrated high-performance of graphene-based electrochemical capacitors, which retain excellent electrochemical parameters under high mechanical loads. Devices made with laser engraved graphene electrodes are characterized by very high energy density in different electrolytes, high power density and postcyclic stabilities. Moreover, these supercapacitors retain excellent electrochemical properties under high mechanical loads, so that they can be used in powerful and flexible electronic devices. Conductivity of graphene electrodes exceeds 1700 S/m, while electrodes on activated carbon have only 10-100 S/m. Due to high mechanical strength, LSG-electrodes can be used in supercapacitors without bonding elements or current receivers, which simplifies design and reduces cost of manufacturing supercapacitors [45].

Some scientists are studying possibility of lithium-ion batteries efficiency increasing (by using graphene as an anode), which will increase their capacity, durability and charge rate. Moreover, graphene is in the process of being studied for use in the production of supercapacitors, which will allow them to charge very quickly and accumulate significant amount of electricity [37].

Specific energy capacity of graphene is 50 times higher than the energy capacity of lithium-ion batteries. Noticing this property, scientists began to develop new generation of batteries. Problem associated with the bulky and limited charge capacity of batteries for electric cars will be solved soon. Car with graphene battery will be able to drive thousand km and it takes about 8 min to charge battery. Charger from Zap & Go takes 5 min to charge smartphone up to 100%. Although test prototype had capacity of only 750 mAh, this result cannot fail to impress.

Next year, the company's engineers promise to reduce this figure to 15-20 seconds. Meanwhile, Huawei has developed conventional lithiumion batteries, which, thanks to use of graphene, can operate at temperatures up to 60 °C that is 10 °C higher than indicator of standard batteries and extends battery life by almost 2 times [35].

The prototype of the new memory device type consists of only 10 atoms of graphene. During laboratory tests, the group managed by American Rice University Professor James Tour created silicon modules, where 10 atomic layers of graphene were placed. Resulting graphene layer got thickness of circa 5 nm. Researchers say that new experimental modules contain basic cells of information storage about 40 times smaller than the cells used in the most advanced 20 nm flesh memory modules. This technology has the potential to increase storage capacity of memory modules many times over. In addition, these memory devices can withstand high radiation and temperatures up to 200 °C, preserving all information. Another advantage of this development is its unprecedented energy efficiency. Memory modules use two initial states for data storage: neutral (off) and charged (on) ones. To encode 1 bit of information in graphene modules, it requires million times less energy than to encode the same bit in silicon chips [46].

In the conclusion of this subsection, note that one of the problems for graphene to be widely used in the mass production of electronic devices is an absence of the sufficient band gap or problem with the gap modulation. The current-voltage behaviour of perfect (defect-free) graphene is symmetrical with respect to the zero-voltage point and thereby does not allow switching of graphene-based transistors with a high on-off ratio. There are several ways for engineering a band gap in graphene. They are: cutting graphene into nanoribbons [47] or nanomeshes [48], applying perpendicular magnetic field to bilayer graphene [49], surface adsorption or/and introducing specific defects [50, 51], using substrate [52, 53], configuring (ordering) of impurity (adsorbed) atoms [54-64], and applying different strains such as uniaxial tensile [65-72] and shear [73] deformations or their combination [74-76].

4.3. Medicine

Graphene, due to its thinness and strength, high electrical conductivity, large surface area, has great prospects for use in development of fast, highly accurate and efficient bioelectric sensors to monitor and regulate such indicators as cholesterol, glucose, haemoglobin levels, and even deoxyribonucleic acid (DNA) sequencing. These substance superpowers in optics and electronics will allow doctors to recognize malignant tumours at an early stage of development. Eventually, we can even see the

constructed 'toxic' graphene, which can be used as an antibiotic and antitumor agent, as well as in tissue regeneration [77]. Graphene oxide is capable of targeted drug delivery to a certain human organ, by passing the surrounding tissues. Recently an announcement about sorbent sensors creation was made. It can recognize DNA molecules using properties of nanomaterial. Researchers of Stephanie Sidlick's team (from Carnegie Mellon University) tested new composition of graphene, which is biodegradable, capable of mimicking bone, attracting stem cells and, ultimately, improving process of skeletal repair in animals. According to other discoveries, the phosphate graphene serves as a frame that allows body's own cells to regenerate missing or damaged bones faster. The method has already shown success on mice experiments. This developing technology could become an important part of orthopaedic medicine, helping us to recover faster, due to stronger and healthier bones. According to Sidlick's group study on graphene, the frame represents a modern approach to orthopaedics; it enters the body to maximize recovery from the inside. When graphene, like a wooden lattice in a grapevine garden is placed on the damaged bone tissue, enveloping it, it serves as a structure to bind and grow bone cells. In contrast to the garden lattice, the graphene frame is destroyed as the bones grow, disappearing after healing of fractured place [78].

The frame approach is not new, but this study shows improvements in design, composition and production of phosphate graphene. Improvednanotechnology methodology contributes to an easy manufactured and used, as well as practical for health product. The frame is also highly customizable; it attracts right calcium ions, has certain tensile strength, and other necessary physical properties can be 'programmed' into the material as it is manufactured to resemble real bone. More importantly, this study showed that graphene 'scaffolds' can work both with and without help of stem cells, in this case, bone marrow stromal cells. Most other forms of regenerative scaffolds relied on these stem cells to accelerate recovery [77].

Among the most 'exotic' applications of graphene (on creation of which researchers from China are currently working), there is the express analysis of DNA. If the way to make such an analysis very quickly and cheaply is found, certainly, it could seriously change health care, and indeed our whole life. The fact is that graphene is a single layer of atoms, in which you can make 'holes' by burning them, *e.g.*, with an ion beam. If then we can drag DNA molecule through such a hole and bring contacts to it, we just have to measure the conductivity, as well as tunnelling current across this molecule. That will be different for each nucleotide. As known, no one has managed to do this yet, but Chinese scientists are actively working on it [78].

4.4. Materials Science

According to information of Korean developers, their patented coating using graphene has excellent flow properties and self-repair capabilities. In the process of experiments, researchers demonstrated that graphene-coated metal restored its structure 200 times after repeated damage and did not corrode in hydrochloric acid solution. Scientists also adding that low viscosity allows material to be recovered very quickly, but such liquids do not adhere well on metal's surface. Overly viscous coatings are either unable to recover at all or do it very slowly. Combining these two contradictory properties in a new coating made it possible to use combination of silicone oil (responsible for fluidity) and reduced graphene oxide microcapsules, which are responsible for the viscosity of substance. Graphene microcapsules form bonded structure by absorbing oil. When it is disrupted, oil comes out of capsules and restores bonds between damage. Researchers decided to use graphene, but any light particles will do as a binder. Authors of invention note that even small concentration of binding particles can significantly increase oil viscosity, e.g., 5 mas.% of microcapsules increased it in thousand times. Particles do not weigh liquid down; so, it does not run off even from a vertical surface. It can be applied to any geometric surface and even in water, without trapping of air bubbles or liquid itself. In addition, resistance of oil with graphene microcapsules to mechanical damage was also tested in acid. Its efficiency turned out to be at the same high level [79].

Scientists from the New York University concluded that the synthesis of bilayer graphene would make graphene into a heavy-duty protective fabric and solve the main problem of all body armour - to combine heavy-duty and lightweight means of protection. Developers around the world will be able to abandon not only from massive steel armour plates, but also in future will abandon to use para-aramid fibre, *i.e.*, Kevlar. Experiments with pressure on two-layer graphene with a diamond rod showed that this material is much better able to withstand any mechanical damage and almost does not deform. The unique properties of graphene, in addition to reducing the weight of body armour, will solve another important problem. At present, a soldier or Special Forces' officer wearing body armour, regardless of protection class and type of armour, when it is hit by pistol or rifle bullet in any case gets severe damage, so-called compression or armour injury. According to scientists, new materials allow protecting the owners of such equipment not only from death, but also from severe health damage. However, usage of graphene in body armour will be associated with some problems. The strength of such a design can be explained through the higher velocity of shock wave propagation in graphene; it dissipates energy much better. Nevertheless,

the problem is that to stop the bullet and reduce the armour impact so far requires an armour plate consisting of many millions of graphene layers. This requires industrial-scale production of this material, which requires a lot of work [80].

Graphene can also be used to obtain new materials, *e.g.*, to fluorinate it, obtaining fluorographene. This is a two-dimensional analogue of Teflon, known to all homemakers, which is used to cover frying pans. However, unlike Teflon, fluorographene is much thinner and stronger. In general, the use of this strong, thin and very chemically inert twodimensional material can be limited only by human imagination [46].

4.5. Automotive and Aviation Industries

Graphene opens wide prospects for the automotive industry, in particular for electric cars. The fact is that vehicles made of graphene have less weight and more rigidity of body, which allows them to accelerate faster and consume much less electricity. As for aviation, weight is everything since the cost of flight directly depends on it. That is why the English entrepreneur Richard Branson (and others, less well-known people) predicts complete transition of commercial airlines to much lighter and stronger graphene in next decade. For example, Airbus has been actively involved in this area for several years. Since graphene has the highest strength and lightness, it is expected to be used to create material to replace steel in construction of aircraft. This will save fuel and will increase flight range by reducing weight. Due to its high degree of electrical conductivity, it could even be used to cover surface of airplane to protect it from lightning strikes. According to scientists, sensors created based on graphene will be able to analyse strength and condition of aircraft, as well as predict earthquakes [45].

4.6. Ecology

With the use of graphene, it is planned to cheapen the process of transformation of seawater into fresh water. The filter will be a graphene membrane with holes so small that they will not let salt particles to go





through. This device will be strong and durable; it can be used for desalination of water in large volumes (Fig. 12) [81, 82].

Addressable sorbents of graphene oxide will be able to deactivate contaminated areas. Now, the application of the product for purification of water resources and air space from radionuclides is being considered. Scientists have developed graphene solution, which absorbs nitrogen oxide from the air, and does it by 70% more effectively than existing methods. Buildings treated with such compound will help if not to get rid of harmful emissions, then, at least make the air cleaner.

New technologies based on graphene oxide will make technological revolution in chemical industry. They will allow reducing significantly the cost of precious metals extraction from poor ores [81].

4.7. Construction

Chemists in the UK have developed technology for graphene producing from discarded car tires; a tenth percent of such material is enough to make concrete stronger by almost in three times. Every year almost a billion old car tires are thrown away around the world. This trash is a serious global problem, and scientists are seeking new ways to recycle and reuse tire materials; in principle, they can even be used to make lithium-ion battery components. Recently, chemists from Rice University have learned to produce graphene from old tires, although of low quality, but suitable for addition to cement mortar and make it into concrete of high strength. Concrete itself is a significant source of greenhouse gases in atmosphere. Therefore, if the use of higher-strength grades can increase operating time of built structures, it will also serve to the benefit of the environment, in addition saving resources. Innovation is based on the 'flash' technology [46]. It allows burning of organic wastes in powerful and short (0.3-1 s) electric discharges, turning them into pure carbon. Carbon atoms form graphene with a turbostratificated, *i.e.*, highly disordered structure, which has many defects. Unlike 'high-quality' graphene, it dissolves better, which facilitates some applications. After recycling, 70% of the original material turns into turbostratificated graphene for addition to cement mortar. Then, scientists went on to test an effect of 'turbostratificated 'flash' graphene' (tFG) on concrete by adding it to Portland cement in amounts ranging from 0.1 to 0.5 wt.%. After curing for just seven days, the material showed by 30% higher compressive strength. The cost of the process in industrial application will be about 100 dollars per ton of the initial material.

Adding of graphene to concrete makes the resulting composite material twice as strong and four times increases its water resistance. According to scientists' investigations, the development will reduce the amount of necessary materials for the production of concrete by almost 50%, which will lead to savings and reduction of greenhouse gas emissions. Meanwhile, concrete with graphene is no longer a laboratory experiment; it can be found in the real world. Graphenano Smart Materials Company has produced graphene panels for cladding a house in Dubai;

they dissipate heat better than traditional materials. In addition, new material has increased durability: manufacturer assures that service life of buildings made of 'graphene concrete' is 50% higher. GrapheneCA Company developed its own version of graphene-based additive in concrete, which was used in the construction of expocentre in Mexico. Due to its improved anticorrosive properties, the material will be especially in demand in regions with humid climates. The main obstacle to the spread of graphene is the complexity of its production. Scientists are constantly inventing new ways to reduce cost and simplify production of material; so, the appearance of widespread graphene buildings technologies is not far. However, so far, this has not happened; the main task of graphene in construction is to protect various constructions from water, chemicals and aggressive environment [80].

Graphene in the architecture of future can become much more than just a construction material. In the future, it will turn each building into small power plant, which will produce electricity and share it with neighbours.

The Hyrdra Skyscraper project entered the Evolo Skyscraper Competition in 2011. Serbian architects decided to use the super-conducting ability of new material to the maximum: according to their idea, graphene shell of spire should collect electrical discharges during lightning strikes, directing them to the accumulators located in the base of tower. By the way, due to graphene electric wiring and even information screens can be applied directly to the surface of buildings, which will radically change the appearance of cities [78].

Another competitive project is floating Graphene Skyscraper. Its author proposes to use seawater as a construction material, pumping it into the graphene membranes [80].

The founders of the Heal-Berg project have gone even further; they want to build a skyscraper completely of three-dimensional graphene, obtained by separation of carbon from carbon dioxide. The building itself will also recycle carbon dioxide, thus fighting climate change. Seawater will be used to cool skyscraper, and authors propose to obtain energy in two ways, namely, with the use of wind turbines and due to the difference in water salinity [81].

Perhaps, the most futuristic project involves usage of graphene to create space elevator. The idea is to connect the Earth surface with orbital station by strong rope, which could be used to deliver people and cargo. Theoretically, only graphene has the necessary properties that would allow the realization of bold idea. Thus, the material, which began with a piece of graphite and duct tape, will one day make space travel accessible to everyone.

5. Conclusions

The article described the properties of graphene, methods of its synthesis and variety of its applications in such areas as energy, electronics, optoelectronics, medicine, bioengineering, aerospace and aviation, ecology, material science, construction *etc*.

Nanotechnology and nanomaterials have attracted increasing research interest over the past 20 years, and the achievements largely depend on the ability to create structures from various materials with different shapes and sizes at the nanoscale and to assemble them efficiently into complex architectures. Against this background, graphene has the greatest potential for use in a wide range of products and industrial applications [20].

Development of metals has radically changed people's life, and the same fate is prophesied for graphene. The path from fundamental discovery to practical results is overcome in a few decades. In the case of graphene, this time was shortened by several months. The ordinary carbon miracle opened new milestones in the world of nanoelectronics. There is no doubt that in a few years, it is with the help of graphene humankind will see revolutionary new devices and technologies [29].

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Received 28.03.2022; in final version, 05.05.2022

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ПЕРСПЕКТИВИ ЗАСТОСУВАННЯ ТА ГЛОБАЛЬНА ЗНАЧУЩІСТЬ ГРАФЕНУ

Оглядова стаття є екскурсом по світових публікаціях, що описують властивості графену, методи синтезу та різноманітність сфер застосування. У статті докладно описується структура графену, а також способи одержання його: мікромеханічне розколювання, хімічне розшарування, епітаксійне зростання та хімічне газофазове осадження, а також переваги та недоліки кожного з них. Окрім того, огляд містить інформацію про електронні, механічні, оптичні та хімічні властивості графену, які надають йому унікальність. Актуальність дослідження полягає в тому, що завдяки своїм унікальним властивостям графен та його модифіковані квазидвовимірні структури є об'єктами підвищеного наукового інтересу в різних галузях науки, таких як енергетика, електроніка, оптоелектроніка, медицина, біоінженерія, аерокосмологія, авіація, екологія, матеріалознавство тощо. Задля розширення читацької аудиторії журналу серед фізиків, хіміків, матеріалознавців, які не є глибокими спеціалістами у графеновій науці, стиль викладання огляду місцями наближено до науково-популярного.

Ключові слова: карбонові алотропні форми, графен, графенові плівки, наноматеріали, мікромеханічне розколювання, хімічне розшарування, епітаксійний ріст, хімічне газофазове осадження, біоінженерія, оптоелектроніка.