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Laser synthesis of graphene in liquid nitrogen

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Abstract. In this paper discusses the properties and methods of obtaining graphene. The processes and mechanisms of graphene formation under the influence of femtosecond laser radiation in liquid nitrogen are considered. Experimental schemes of laser-induced graphene exfoliation in liquid nitrogen are presented.

1. Introduction

Carbon is one of the paramount substances necessary for life on our planet. Due to the ability of carbon atoms to connect in various ways, carbon-based systems exhibit various allotropic structures and properties. Since ancient times, certain allotropic states of carbon, such as diamond and graphite, have been known. With the emergence of the term "nanotechnology", quoted in a lecture by Nobel laureate R. Feynman called "There is plenty of room at the bottom" [1], new methods of imaging substances at small scales, leading to the discovery of fullerenes. Discovery of fullerenes by R.E. Smalley, H. Kroto, and R.F. Curl in 1985 sparked an interest in nanoscience, bringing it to the fore.

The results were the discovery of carbon nanotubes by S. Iijima in 1991. However, there is earlier evidence of the discovery of carbon nanotubes, for example, in 1974–1976 [2]. Works have been published that describe thin tubes with a diameter of less than 100 Å made by the method of vapor condensation, but a more detailed study of the structure has not been carried out.

Interestingly, the two-dimensional form (graphene) was obtained quite recently and immediately attracted much attention. The first attempts to obtain a two-dimensional carbon structure were made long before the discovery of "real graphene". For example, in 1962, the name graphene was born, when Hanns-Peter Boehm described the properties of carbon one atom thick [3]. In the works of Peierls and Landau (1935–1937), it was said that strictly two-dimensional (2D) carbon crystals are thermodynamically unstable and cannot exist [4, 5]. This was one of the reasons why no one tried to obtain two-dimensional crystals before their discovery. Thermodynamic stability turned out to be possible due to thermal fluctuations that create a "ripple" – a waviness of the graphene surface with a height of ≈ 5 nm. The discovery of real graphene occurred in 2004, after publication in the journal Science [6], wherein it was reported about getting carbon monolayer was on an oxidized silicon substrate by dint of mechanical splitting. This technique consists in peeling graphene scales as a result of friction of crystalline graphite against each other, or in "peeling off" them from the surface of graphite using a special adhesive tape with its subsequent dissolution.

Graphene is a single-layer two-dimensional carbon structure organized into a regular hexagonal crystal lattice with carbon atoms at the vertices arranged in plane. Graphene has a layer thickness of one atom, and the distance between them is 0.142 nm, with each atom associated with three neighboring atoms with covalent chemical σ -bonds with sp^2 -hybridization, and the fourth valence



electron is included in the conjugated π -system of graphene. Thus, three bonds located in the plane define the geometric structure of graphene, and the fourth, its unique electronic properties.

2. Properties of graphene and methods of synthesis

The most attractive feature of graphene is its unique properties. This material is the first known two-dimensional atomic crystal [7]; the thinnest object ever received; the most durable material [8]; charge carriers in it are massless Dirac fermions [9–11]; it conducts electricity very well [12] and heat [13]; very elastic and impenetrable for many molecules. Graphene has a huge number of different properties, a detailed review of which is impossible to give in this work. For this reason, only certain properties will be considered.

2.1. Optical properties

The optical properties of graphene are very paradoxical, since graphene is one atom thick, and it absorbs most of the light. In the infrared limit, the absorption coefficient is $\pi \alpha \approx 2.3\%$, where $\alpha = e^2 / \hbar c$ is the fine structure constant, corrections to this value in the visible spectral range are less than 3%. Such a noticeable absorption coefficient makes it possible to see graphene with an unaided eye. This is the paradox, since graphene is the smallest particle. At higher frequencies, the absorption increases, reaching 10% due to the Van Hove singularity at the edges of the zone. The optical absorption of graphene can be changed by shifting the positions of the Fermi level by adjusting the concentration of charge carriers [14].

2.2. Linear dispersion dependence and chirality

Graphene is a semimetal with a zero forbidden band, since the valence band and the conduction band touch at two points K and K'. Such an electronic structure is a consequence of the hexagonal symmetry of the lattice, and it does not apply to Bravais lattices, since it contains two atoms in each unit cell. The carbon atom orbitals hybridize to form zones, the intersection of which at points K and K' forms a gapless spectrum with a linear dispersion. Consequently, the absence of a gap between the valence band and the conduction band of graphene is very stable and is a consequence of the symmetry between the sublattices.

Linear dispersion itself makes graphene special, but not limited to this. The symmetry and charge conjugation of the electron-hole pairs present in graphene determine the chiral characteristics of pairs of charge carriers. The specificity of chirality is due to the pairwise inequivalent sublattices of the crystal structure of graphene. Such properties of graphene allow one to “see” the relativistic effects of quantum electrodynamics (QED).

2.3. Klein paradox

The Klein paradox, theoretically predicted in 1929, is the visual result of the chiral symmetry of quasiparticles in graphene [14]. The paradox is associated with an increase in the tunneling of a relativistic particle approaching unity, when the barrier height exceeds $2m_0 c^2$ (where m_0 is the rest mass of the particle, c is the speed of light). This can be viewed as a consequence of backscatter suppression, since massless relativistic particles, such as photons, always move at a constant velocity – the speed of light, whereas backscattering requires that the speed at the turning point is zero. One can also consider the birth and annihilation of particle-antiparticle pairs, which in regions of a strong electric field are due to the Schwinger mechanism.

The Klein paradox for chiral quasiparticles in graphene leads to the transformation of an electron inside a potential barrier into a hole and to an equal unit probability of tunneling through such a barrier, at least during normal incidence. This, in turn, leads to the absence of localization and the final minimum conductivity even in graphene with moderate disorder, which in the limit of the formally zero concentration of charge carriers breaks up into electron-hole puddles. The absence of backscattering, leading to the Klein paradox, also provides a positive sign of quantum (interference) corrections to conductivity, leading to weak anti-localization.

2.4. *Quantum Hall effect*

Quantum Hall effect occurs in graphene under normal conditions, that is, at room temperature and magnetic fields [15]. Measurements of the transverse resistivity of the Hall demonstrate the ambipolarity of the current-voltage characteristic of graphene. It is manifested in the fact that electrons and holes carry current together, being chiral, have half-integer spin indices, different in signs, and are located in adjacent, adjacent valleys – between the points of Dirac. The mechanism of ambipolar electrical conductivity is due to the mutual conjugation of electrons and holes and the properties of graphene as a semimetal associated with this conjugation. Ambipolarity means the ability to control the type of carriers of another sign (by switching electrons and holes) and is a remarkable property of the current-voltage characteristics of the transistor inclusion of graphene.

2.5. *Methods of graphene synthesis*

A carbon monolayer was first obtained by micromechanical cleavage technique of crystalline graphite [6, 7]. This technique consists in separating graphene sheets from crystalline graphite, either as a result of friction of small graphite crystals against each other, or with the help of adhesive tape, the subsequent dissolution of which results in individual graphene layers. Studies show that this technique allows you to select single-layer graphene sheets, having an ordered structure and having about 10 microns in width and about 100 microns in length.

The main problem with this method is the difficulty of identifying the resulting graphene, since the number of layers varies from one to one hundred. To identify such objects, standard observation methods based on the use of scanning probe microscopy, which does not allow determining the number of layers of a multilayer structure, are unsuitable. The use of an optical microscope was a solution on the way to identifying and obtaining samples of single-layer graphene.

The chemical vapor deposition (CVD) method is widely used for the synthesis of carbon nanostructures. Before the appearance of nanocarbon materials, used to produce thin carbon filaments, later found application for the synthesis of carbon nanotubes in macroscopic quantities. The essence of this method is the thermocatalytic decomposition of gaseous hydrocarbons on the surface of some metals to form different nanocarbon structures [16].

The laser ablation method is based on the removal of matter from the surface by a laser pulse. Obtaining graphene by this method is based on the stratification of crystalline graphite under the influence of laser radiation. As a target, a crystal of highly ordered pyrolytic graphite is used, which is placed on a silicon substrate. Graphene synthesis is carried out in argon atmosphere. Carbon particles formed as a result of laser ablation of the graphite surface fall on a silicon substrate. When the energy density of the laser radiation on the target is from 1 to 10 J/cm², thin scales appear on the surface of the target, which spontaneously separate from the target and fall on the surface of the substrate.

3. **Method of graphene laser-induced synthesis in liquid nitrogen**

The main idea of method is the effect of femtosecond laser radiation on a graphite sample immersed in a liquid nitrogen medium [17]. The physical meaning lies in the heat-conducting property of graphite, as well as the change in its structure at low temperatures. The thermal expansion of the graphite lattice is anisotropic; it manifests itself more strongly if the lattice order is higher. In the direction perpendicular to the basic planes, the coefficient of thermal expansion is positive, practically independent of temperature, and more than 20 times higher than the average absolute value for the basal planes. Consequently, the temperature coefficient of linear expansion in the direction of the basal planes is much less than in the perpendicular direction, thereby contributing to the separation of the structure with intensive heating.

3.1. *Experimental setup*

To obtain graphene samples by the method of laser synthesis in liquid nitrogen an experimental setup was developed (figure 1). For the experiment, a double-circuit cryostat with vacuum thermal insulation was also developed. The design of the cryostat made it possible to eliminate such

difficulties during the experiment as: boiling of liquid nitrogen during heat exchange with the external environment; cooling and maintaining a low sample temperature; icing glass windows. Liquid nitrogen was used as a source of low temperatures; it is also possible to use other cryoagents.

The cryostat design is a steel cylindrical vessel equipped with transparent windows through which observation or introduction of laser radiation into the vessel volume can be carried out (the glass used is transparent for the working wavelength of laser radiation). The product is equipped with two independent circuits, allowing to work in different temperature ranges, as well as to place samples in different environments (liquids, gases). The assembly of the product is carried out by means of threaded connections. At each butt section of the flanges a special polytetrafluoroethylene gasket is installed. The unit has an object table, on the surface of which there are threaded holes for reliable fastening of the sample. The object table is made of a material with high thermal conductivity to ensure good heat exchange with the sample. The design of the cryostat provides an additional scheme for the removal of combustion products.

The carbon sample is processed by a pulsed femtosecond Yb:KGW laser system TETA-10. A sample of carbon is placed in a cryostat. After creating the vacuum in chamber, liquid nitrogen is supplied to the cryostat and laser treatment is performed. Removal of products of combustion and vapors of liquid nitrogen is carried out through the ventilation system. Liquid nitrogen is removed from carbon materials in an evaporator equipped with a substrate for the deposition of graphene.

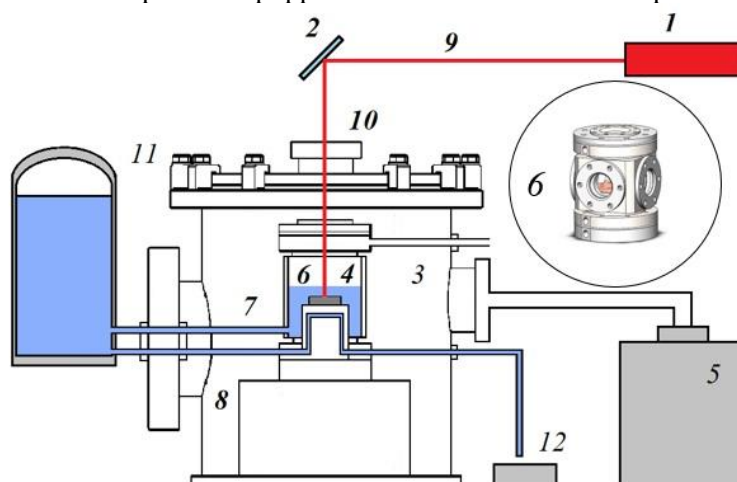


Figure 1. The experimental setup: 1 - laser, 2 - mirrors system, 3 - ventilation system, 4 - carbon sample, 5 - turbomolecular pump, 6 - cryostat, 7 - liquid nitrogen supply system, 8 - vacuum chamber, 9 - laser radiation, 10 - input window of laser radiation, 11 - insulating vessel, 12 - nitrogen evaporator.

3.2. Mechanisms of graphene exfoliation

Under normal conditions, the distance between the atoms of graphite is 1.42 Å, and the interplanar distance is 3.38 Å. When graphite is immersed in liquid nitrogen, it is cooled. Low temperature leads to a decrease in lattice vibrations of the source material of graphite; therefore, the interplanar distance decreases to 3.393 Å, and when heated increases to 3.465 Å [18]. The diameter of the liquid nitrogen molecule is approximately 0.32 Å, which is less than the interplanar distance of the cooled graphite. This dependence allows the nitrogen molecule to penetrate into the interplanar distance of graphite, through cracks, chips and delaminations.

The nitrogen molecule is heated at laser pulses, where the main process is the transfer of energy through a sample of graphite - a molecule, due to thermal conductivity. During a laser pulse, electrons transfer energy to the lattice of the substance, and it heats up in the laser-induced area. As a result of laser heating and, as a result, an increase in the amplitude of vibrations of nitrogen molecules, a

volume expansion of the region occupied by nitrogen molecules occurs (transition from the liquid phase to the gas phase). Thus, interplanar carbon π -bonds (16–40 kJ/mol), weaker than σ -bonds ($\approx$ 450 kJ/mol), are destroyed. Effective heating of nitrogen is due to the transfer of thermal energy from the graphite lattice due to the absence of nitrogen absorption bands at the working wavelength.

For successful application of laser exfoliation of graphene it is necessary to provide special conditions for cooling the laser exposure zone. Laser interaction on the target in the cryogenic medium forms a larger temperature gradient, which increases the thermoelastic stresses. A schematic representation of the process of laser separation of graphene is shown in Figure 2.

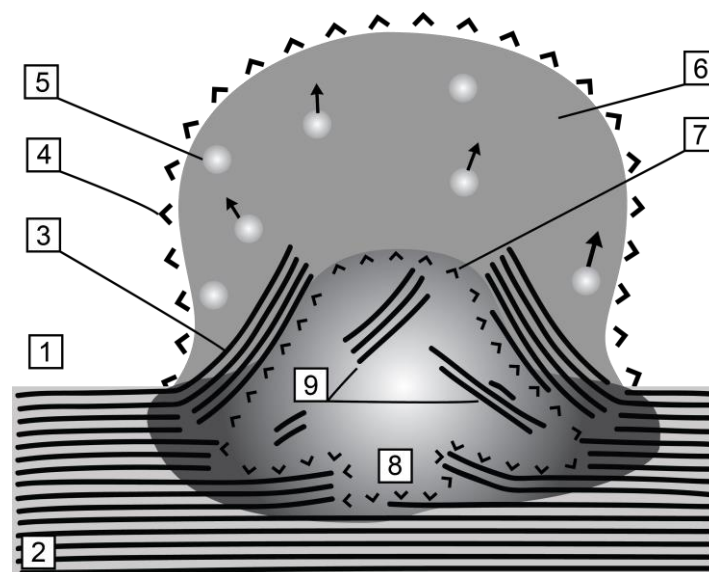


Figure 2. Schematic representation of the flow processes: 1 – liquid nitrogen, 2 – carbon target, 3 – exfoliating graphene, 4 – propagation front of vapor-gas region, 5 – evaporated nitrogen, 6 – vapor-gas area, 7 – front of high-pressure region, 8 – high-pressure area (the heating of intercalated nitrogen, laser ablation), 9 – exfoliated graphene

At the interaction of ultrashort laser pulses with a graphite sample in liquid nitrogen, several variants of the processes of structural changes in the material can be distinguished. When the laser radiation power is insufficient for laser ablation processes, the energy of photons is absorbed by the carbon lattice and intercalated nitrogen. Weak interplanar π -bonds are destroyed due to a sharp increase in lattice vibrations and nitrogen molecules.

When energy of laser radiation in excess of the ablation threshold is the destruction of the graphite surface in the affected area. As a result of the processes occurring during laser ablation, a high-pressure region is formed on the walls of the formed cavity. The stratification structure of the graphite to multilayer graphene in this mechanism is the result of a reaction effect of ablation products.

3.3. Results of experiments

Processing of carbon targets surface was carried out by femtosecond laser system TETA-10 with following parameters: wavelength $\lambda = 1030$ nm, radiation pulse duration $\tau = 280$ fs, pulse repetition rate $f = 10$ kHz, pulse energy $E_{\max} = 150$ μ J. Surface processing of graphite was carried out in liquid nitrogen, which covered it with a layer 10 mm thick. The diameter of the laser spot on the target surface reached 100 μ m. As the source samples to obtain graphene was used, the target of highly oriented pyrolytic graphite HOPG-1,7-10x10x1-1 and glassy carbon SU-2000.

After processing graphite in liquid nitrogen, the obtained samples were studied to confirm the result. The result of the separation of graphene on the surface of HOPG is demonstrated on Figure 3.

Obviously, the separation begins from the center of the crack in accordance with the mechanism described above. SEM-images show that some structures flake and bend in the direction from the beginning of the separation remain at the base, and in some places also flake. The next stage of using the obtained graphene sheets is the separation from the original sample using ultrasonic treatment, the formation of a solution and deposition on the required substrates.

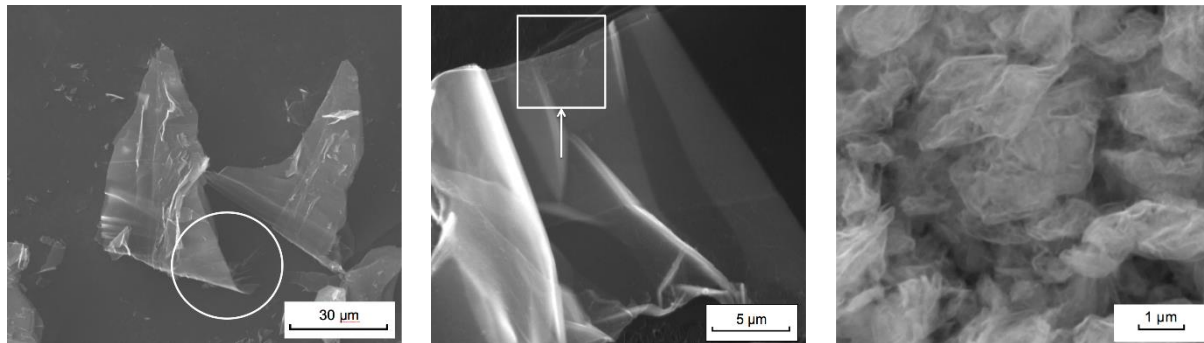


Figure 3. SEM-images of graphene layers

4. Graphene application

The most attractive feature of graphene is its properties, which are superior to those of competing materials. This makes it perceptible for many applications. One of the promising areas is the use of graphene as a porous electrode for supercapacitors. The use of graphene as an electrode material in electrochemical supercapacitors is shown in [19]. The authors used graphene obtained by three independent methods. The first method involved thermal exfoliation of graphitic oxide. In this method, graphitic oxide was prepared by reacting graphite with concentrated nitric acid and sulphuric acid with potassium chlorate at room temperature for 5 days. Thermal exfoliation of graphitic oxide was carried out in a long quartz tube at 1050°C. In the second method, graphene was obtained by heating nanodiamond at 1650°C in a helium atmosphere. The last method involved the decomposition of camphor over nickel nanoparticles. The reaction was carried out in a two-stage furnace and the camphor was slowly sublimed from the first furnace to the second furnace held at 770°C where the micron sized nickel particles were placed.

The results obtained in [19] showed that the use of graphene as an electrode for supercapacitors is possible and promising. Since the specific capacity of exfoliated graphene in an aqueous electrolyte is comparable with the capacity obtained with activated carbons, and exceeds the capacity of carbon nanotubes, while the value of the energy density of graphene capacitors is one of the highest.

5. Conclusion

The basic properties of graphene and methods of its production are considered. The experimental schemes and software for the complex of femtosecond laser processing of materials have been modernized to investigate the influence of processing conditions and raw materials on the nature of the formed nano- and microstructures. Specialized cryostat for laser synthesis of graphene has been developed. It is shown that common mechanism of graphene exfoliation under femtosecond laser action in liquid nitrogen is separation of carbon surface layers in samples as a result of the disturbance of interplanar bonds due to the expansion of intercalated nitrogen into the gas phase under laser heating.

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