Overview of the graphene production technologies and instrument application

Alexander Alexandrovich Lebedev[1], Pavel Victorovich Bulat[2]

[1] Joffe Physical Technical Institute, Polytechnicheskaya str., 26, St. Petersburg, 194021, Russia
[2] Saint Petersburg National Research University of Information Technologies, Mechanics and Optics, (University ITMO), Kronverksky pr., 49., Saint Petersburg, 197101, Russia

Abstract. Analysis of the national and foreign publications dedicated to the graphene production, its properties study and graphene-based device prototyping. It is demonstrated that one of the most attractive devices for practical realization is a gas sensor based on the graphene film. Also it is demonstrated that a method of silicon carbide thermal decomposition is the advanced technology for the graphene electronics realization.

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Introduction

Over the last years, interest in production and study of planar nanocarbon layers (graphene) has grown. Graphene, a two-dimensional crystal, consisted of one (or few) layers of carbon atoms connected with sp^2 bonds into hexagonal two-dimensional crystal lattice (fig.1).

Among the graphene benefits there are current carrier high mobility (~10^4 $cm^2/(B•c)$) at room temperature, high mechanical strength, combination of transparency and low electric resistance. These layers are stable at room temperature in air and can be used for nanotransistors creation.

Use of graphene as the component base for the future nanoelectronics will allow to overcome the constrains peculiar to the traditional silicon electronics and related to device miniaturization and power consumption level. Company INTEL considers the graphene as a possible base for microelectronics in the future and as a possible silicon replacement in integrated circuits.

The work objective is, based on well-known literature sources, selection of a device which is possible to create based on the graphene film and which is more close to industrial realization. At the presence, there are several graphene technologies which significantly differ for the product film quality and its geometry. Thereby, one of the work objectives is selection of the graphene growth technology which can produce the best material to meet manufacturing a device selected earlier.

A and B are triangle subgrids forming the graphene hexagonal crystal lattice. E is a wave function, κ is a wave vector, a is the lattice characteristic dimension (distance between two adjacent atoms, γ_0 of the adjacent atoms interaction energy).

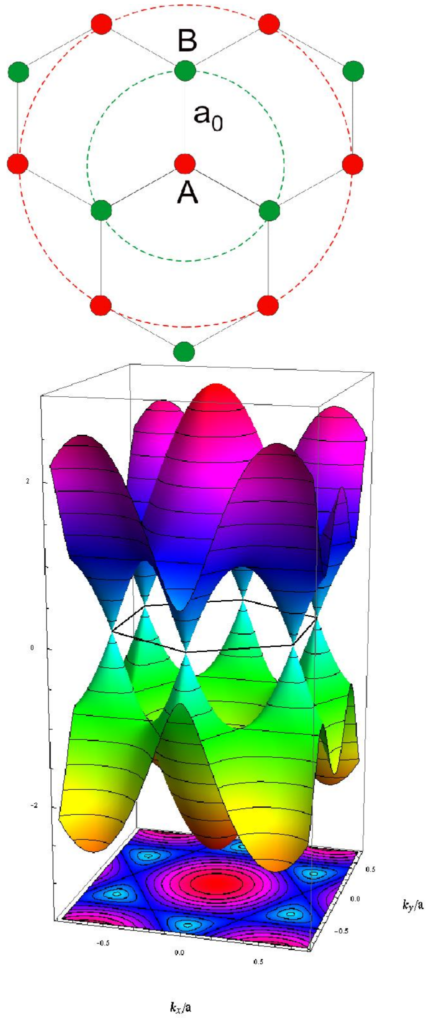

Fig.1. Graphene band structure

As we know, the graphene (carbon two-dimensional layers) was discovered by Andrei Geim and Konstantin Novosyolov, scientists of Russian origin, who were awarded a Nobel Prize 2010 in

Physics for their discovery which provoked a surge of publications on this subject. The range of the graphene possible applications covers development of field transistors for digital and analog electronics, nanoelectromechanical systems, quantum dots, cold cathodes, super capacitors, gas sensors, almost transparent electrodes and coatings. Capabilities of use graphene for hydrogen storage and composite creation are studies also. As two-dimensional material the graphene provides the absolute limit of miniaturization in one dimension, and is a suitable base for lithographic manufacturing of different nanoelectronic, nanomechanical and nanochemical devices.

It should be noted that number of theoretic and experimental works on the graphene study are related as 1: 10. If to speak about the development and research of pilot devices, this ratio becomes even more for benefit of the theory. Let`s consider the basic types of the devices to be developed.

Transistors

The most direct application of the graphene as the base for nanoelectronics is using it as a material for the field-effect channel which is analogous to modern MOS-transistors (Fig. 2).

The principle of such a device is based on the field effect: changing the concentration of charge carriers in the graphene using gate voltage it is possible to control the graphene conductivity which is in approximate proportion to the concentration [1].

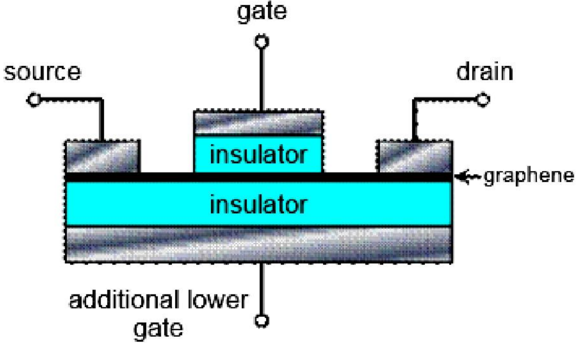

Fig. 2. Diagram of a simple field transistor based on graphene

The graphene sheet serves as a channel connecting the source and drain, while the gate electrodes control the concentration of carriers in the graphene and, consequently, its conductivity.

Many experimental groups all over the world have made considerable efforts for manufacturing and studying such devices [2]. Advantages of the graphene transistor are rapid response and low heat generation provided with high movable charge carriers.

Although the carriers mobility in the graphene suspended samples achieves very high values (up to 200 000 cm^2/B·c), the graphene conductivity in the field transistor composition is significantly limited with impurities and disorder in the substrate and gate electrode. However, even in such conditions the typical values of the carrier mobility exceed the ones for silicon by one or two orders making up a few hundred to thousands cm^2/B·c (Fig.3).

Another serious advantage of the graphene is possibility of miniaturization of graphene devices up to nanometric dimensions (Fig.4), while silicon stops its existing as a crystal at dimensions less than 10 nm.

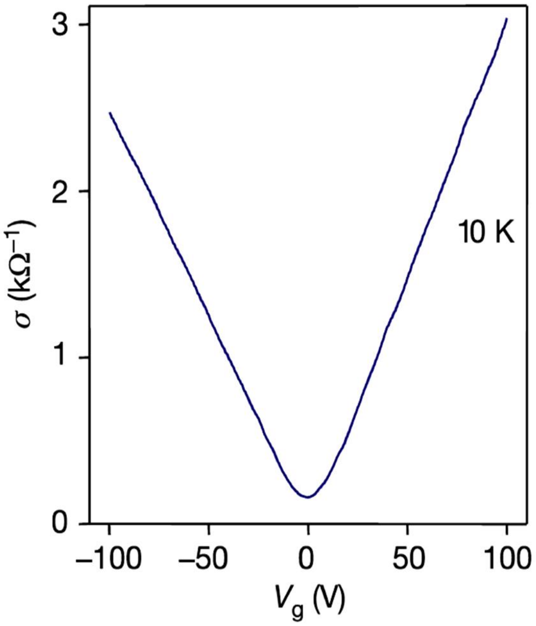

Fig.3. Dependence of the channel conductivity on the gate voltage. σ = neμ, μ – mobility of charge carriers (in the graphene at room temperature 2x10^5 cm^2/B·c, n – number of carriers, e – carriers charge

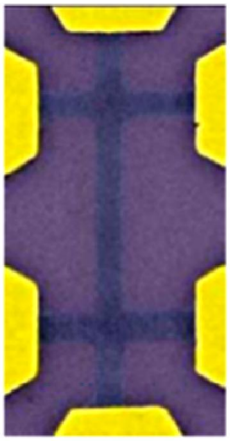

Fig.4. Graphene field transistor (FET) can have nanometric dimensions. View of the graphene transistor under the electron microscope

The key disadvantage of the graphene field transistor is low resistance in the blocking state. The reason lies in absence of a slot in the graphene energy spectrum which leads to the existence of the finite minimal specific conductivity of the graphene even without doping. Moreover, random charges in the substrate generate local nonzero density of the carriers at cumulative absence of the graphene doping. Because of strong conductivity in the blocking state, the graphene field transistor is not very suitable for digital electronics.

There are a few ways to create a slot in the graphene spectrum necessary for the transistor complete blocking. One of such ways is the spatial confinement creating a slot in the energy spectrum of graphene nano-ribbons. However, the slot size and presence depend on the type of the nano-ribbon edge and its width. At whole, the slot value is inversely with the ribbon width.

It is possible to use as a material for the transistor channel the two-layer graphene (Fig.5) which energy field creates a slot with regulated width [3]. However, the value of slot in devices manufactured and researched experimentally up to date is smallish (a few MeV) which allows to block transistors only at low temperatures.

Another way to create a slot in the single-layer graphene is influence of a commensurate crystal substrate dependently on atoms in different graphene sublattices [4]. Particularly, in the single-layer graphene on the silicon carbide substrate a significant slot as large as 260 MeV [4] was observed. It is worth noting that creation of a forbidden band in the graphene usually causes degradation of the mobility which is the main advantage of the graphene for this kind of devices.

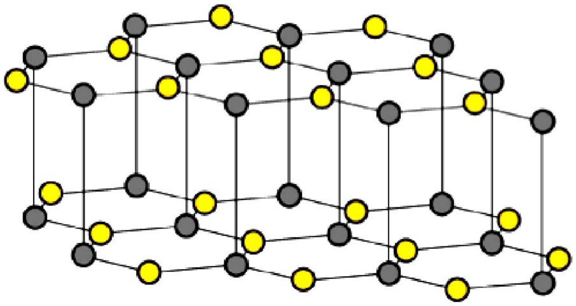

Fig.5. Two-layer grapheme

Absence of a slot in the spectrum of the clear single-layer graphene makes it not suitable enough for use as the transistor base in digital electronics. However, transistors for analog electronics (particularly, RF transistors) do not need complete blocking, and the graphene is very suitable for them. The most important for RF transistor performance is the channel transportation qualities (high mobility and high max speed of carriers) and small scale of its length. The graphene, in virtue of its atomic thickness and good crystal structure, is ideal for these requirements. In experimentally realized prototypes of such transistors maximal operating frequency achieved tens gigahertz. To increase the operating frequency in the latest experiments, transistors with the channel smaller length has been manufacturing. For the channel length less than 100 nm, the transistor operating frequency achieves hundreds gigahertz, which considerably exceeds the silicon transistor best indexes [5, 6, 7].

Capacitors

Development of electrical capacitors of high capacity is topical for solutions in the field of energy storage and transfer. For the simple plane capacitor a critical parameter is the plate's distance which should be as short as possible. As the graphene is the thinnest material in nature with high conductivity and good chemical stability, it is possible to manufacture super capacitors with record capacity on its base.

Capacitors made of both a graphene layer and nearest metal electrode [8] and two graphene layers [9, 10] were studied experimentally. In the work [10] the graphene layers were separated with insulating nanoparticles with dimensions about 10nm which led to the record high specific capacity.

Spin electronics, plasmonics and optoelectronics

One of the possible uses of the graphene in the nearest future in the field of nano electronics is use of graphene layers and graphene nanoribbons for connection of electronic components in chips. Even irregular structures of many graphene layers can provide advantage over traditional metal connections related to heat generation, conductivity, and elasticity and integration level. Moreover, the important strategic advantage of carbon over metal is its availability and low price.

Recently, the nanoplasmonics has been booming in the field of research of surface plasmons and plasmon-polaritons which excitation and detecting can be used for solution of different fundamental tasks and applications. Particularly, using surface plasmons it is possible to transfer large amounts of information in chips, and carry out different electronic optical switching. The graphene is prospective enough as a material for nanoplasma devices as it has many advantages over traditional gold and silver [11]. Electrical doping and chemocal modifications of the graphene allow considerably change its optical properties. Due to its uniqueness, the graphene operns a way to the quantum plasmonics operating with individual quantums of plasmons.

Already they offer different graphene electrical optics practicing nanoplasmonics principles, particularly, optical electronic switches [12], plasma wave guides, super lenses [13], and terahertz lasers [14].

Attraction of the graphene as basis for spin electronics is conditioned by weak spin-orbital interaction and very small hyperfine-structure splitting of electron levels resulting in weak spin current decay. Besides, the graphene zigzag edges demonstrate ferromagnetic properties which can be used for creation of spintronic devices.

Gas sensors

The graphene structure has gas specific affinity [1]. If to place it into the ammonia or nitrogen dioxide impure air, gas particles adsorb (or ‘get stuck’) in it. At the same time, it increases or decreases electrical resistance of the graphene layer. The sensor operation is based on this change measurement.

As we know, the conductor resistance is specified by both the concentration of charge carriers and their mobility. Associate gas molecules, in dependence on their charge and conductivity type of the graphene film, behave like donors or acceptors. That is, they change the concentration of movable charge carriers. Also, adsorbed molecules create additional centers of dispersion and change mobility of carriers.

The graphene detector is easy to be cleaned. Pass current about 10 mA though it, it is enough to heat the structure to initiate desorption of gas particles. Such a cleaning mechanism cannot influence the level of the gas detecting effectiveness: the gas sorption-desorption process is reversible fully, i.e. this is a reusable detector. This makes the technology less energy consuming: you do not need an outer heat source for the detector cleaning.

Moreover, linear dependence of the film reaction on the recorded gas concentration was observed. [15,16]

Earlier, the graphene sensitivity to molecules H_2S, NH_3, NO_2, CO, CO_2, O_2 was observed. The graphene film recorded (Fig.6) on ultralow concentration of different gases less than 1 ppb (part per billion).

The test demonstrated that the graphene ‘feels’ ammonia up to a thousand ppm for 5—10 minutes at room temperature and atmospheric pressure. In this case, the recorded change makes up 30%. Modern commercially available polymeric sensors are significantly worse: 30% change in resistance is achieved in 5—10 minutes in air with 10 000 ppm of ammonia. The graphene detector sensitivity is enough to identify 20 ppm of ammonia in air. Besides, a number of the latest detectors are power consuming: for operation they should be heated up to high temperature, the graphene film successfully works in the standard conditions.

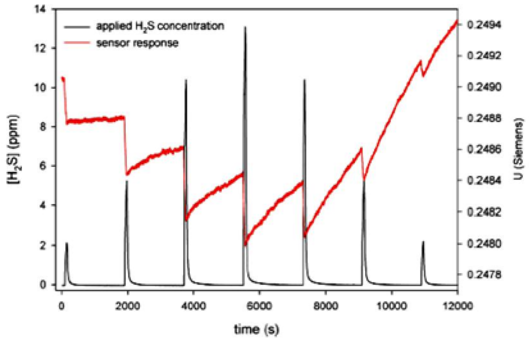

Fig. 6. Typical operating characteristic of the graphene gas sensor

Ammonium nitrate is a component of many explosives. During storage it decays gradually, and emits ammonia in trace quantity, therefore just ammonia detectors are used to search explosives. Honestly, ammonia is used not only for military purpose: this is a component of some processes in the chemical and pharmaceutical industries. Therefore it is necessary to control this gas concentration in the shop air for leakage.

Also you can use the graphene to record different biomolecules [17, 18]

They name two main reasons of high sensibility of gas sensors based on the graphene.

In the graphene, like in a two-layer material, every atom can interact with gas molecules. I.e., the detector useful area / detector volume max ration is achieved.

The graphene two-dimensionality also results in suppressing of carriers fluctuation which considerably decreases different noise of the device.

All these make the graphene very attractive material for gas sensor manufacturing. To manufacture a simple sensor you need just a graphene band with two contacts and chips for resistance measurement. To increase the stability of sensor operation and to decrease noise, detectors are made in the field transistor circuit (Fig.2) [19]. It requires additional development of the technology of thin layer formation in the gate dielectric (SiO_2 is possible).

Data analysis by methods of graphene manufacturing

There are a few methods of graphene manufacturing: flaking-off a piece of graphite, growing on the SiC surface by sublimation method, chemical deposition on the metal surface etc. (see Table 1).

Table 1. Comparison of perspective industrial application of the graphene films manufactured under different technologies.

Technology	Existing disadvantages for industrial application
Mechanical flaking off	Films with irregular form and small area
Chemical intercalation	Not controlled thickness of the films received. Often there is no complete film splitting, 'book' like specimens.
Metal surface deposition	For device creation, it is necessary to separate the film from the metal surface and to transfer it on the dielectric substrate. In this case the graphene property considerably get worse
Electrochemical methods	Uncontrolled forms and sizes of the films received
Thermal decomposition of the silicon carbide surface in the inert gas	Mobility of the charge carriers is less than mobility in the films received by the flaking off method. No other disadvantages.

The graphene layers received by the flaking off method have the structural perfection. However, these layers have micro size and irregular geometrical form. It makes them not very usable for industrial application.

The second place is taken by the graphene films on the silicon carbide surface due to its structural perfection and electrophysical parameters. During SiC heating up to 1300°C in ultrahigh vacuum the silicon is sublimated which results in the graphene layer creation on the crystal surface (Fig.7).

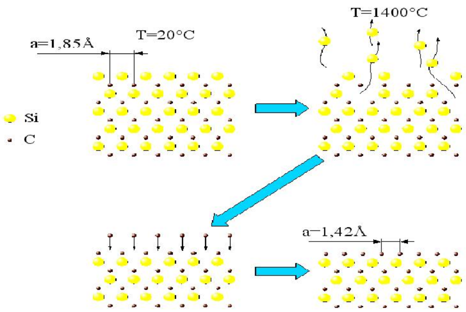

Fig.7. Graphene creation on the SiC substrates

Such films can be grown on the 3 inch SiC substrates and demonstrate uniformity of parameters all over the plate surface. Such plates can be used in the standard technological line for manufacturing of semiconductor devices. Additional advantage of this technology is a possibility to receive the graphene film on semi-insulating SiC substrate which cancels the necessity to transfer the grown film onto the dielectric substrate, like for growing on Mo and other metals.

Advantage of the SiC thermo-destruction method is also low cost and high structural perfection of the received graphene films. This technology is considered as the most perspective for the industrial application. Only the graphene films received by flaking off and thermo-destruction had quantum effect of Hall [20]. All other technologies give films with worse structural perfection. The technology based on SiC thermo-destruction is now considered as the most perspective from the point of view of industrial application in electronics. At the same time, in the Russian Federation there are no researchers (except for this work authors) developing this technology.

Conclusion

This work covers the main information about the graphene characteristics which make it attractive for application in semiconductors of new generation. The perspectives and problems of use of the graphene in field transistors, capacitors, consentration sensors, spin tronics etc. have been considered. The review of the graphene manufacturing lab methods is given.

Summary

The reference analysis demonstrated that the most close to practical application device based on the graphene is a gas sensor. The graphene application allows to achieve superior sensitivity: up to one ppm. This device combines relative simplicity of manufacturing with the wide spectrum of application. It is necessary to notice that the gas sensor structure actually reproduces the field transistor structure. Therefore, the gas sensor can be considered as the first stage in development of complicated transistor electronics based on the graphene.

The analysis of works under the graphene manufacturing methods demonstrated that the most perspective technology for electronics is the thermal decomposition of the silicon carbide surface. Although, the films received under this technology are less movable than the films received by flaking off, they have predicted sizes and easy meet the existing manufacturing lines of semiconductors.

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Corresponding Author:

Dr.Lebedev Alexander Alexandrovich
Joffe Physical Technical Institute
Polytechnicheskaya str., 26, St. Petersburg, 194021, Russia

References

1. K.S. Novoselov, A.K. Geim, S.V. Morozov, D. Jiang, Y. Zhang, S.V. Dubonos, I.V. Grigorieva and A.A. Firsov, 2004. Electric field effect in atomically thin carbon films. Science, 306, 666.
2. McCann E., 2006. Asymmetry gap in the electronic band structure of bilayer grapheme. Phys. Rev. B, 74, 161403.
3. Lemme M.C., 2009. Current status of graphene transistors. Solid State Phenomena, 156, 499.
4. S.Y. Zhou, G.H. Gweon, A.V. Fedorov, P.N. First, W.A. De Heer, D.H. Lee, F. Guinea, A.H. Castro Neto and A. Lanzara, 2007. Substrate-induced bandgap opening in epitaxial grapheme. Nature Materials 6, 770.
5. Chen L. L Y., X. Zhang, P. Yu and Y. Ma, 2010. Electrophoretic deposition of graphene nanosheets on nickel foams for electrochemical capacitors. J. Power Sources 195, 3031.
6. Du X.A., P. Guo, H.H. Song and X.H. Chen, 2010. Graphene nanosheets as electrode material for electric double-layer capacitors. Electrochimica Acta 55, 4812.
7. Wu Z.S., D.W. Wang, W. Ren, J. Zhao, G. Zhou, F. Li and H.M. Cheng, 2010. Anchoring hydrous RuO(2) on graphene sheets for high-performance electrochemical capacitors. Adv. Funct. Mater. 20, 3595.
8. Cheng R., Y. Lin, S. Jiang, Y. Qu, Y. Huang and X. Duan, 2010. Sub-100nm channel length graphene transistors. Nano Lett. 10, 3952.
9. Wu Y., Y. Lin, K. Jenkins et al, 2010. RF performance of short channel graphene field-effect transistor. Tech. Dig. of Int. Electron Device Meeting (IEDM), 226.
10. Schwierz F., 2010. Graphene transistors. Nature Nanotech. 5, 487.
11. Koppens F.H.L., D.E. Chang and F.J. García de Abajo, 2011. Graphene plasmonics: A platform for strong light-matter interaction, http://arxiv.org/abs/1104.2068.
12. Bludov Yu.V., M.I. Vasilevskiy and N.M.R. Peres, 2010. Mechanism for graphene-based optoelectronic switches by tuning surface plasmon-polaritons in monolayer grapheme. Europhys. Lett. 92, 6800.
13. Daas B.K., K.M. Daniels, T.S. Sudarshan and M.V.S. Chandrashekhar, 2010. Polariton enhanced IR reflection spectra of epitaxial graphene on SiC, http://arxiv.org/abs/1010.4080.
14. Dubinov A.A., V.Ya. Aleshkin, V. Mitin, T. Otsuji and V. Ryzhii, 2010. Terahertz surface plasmons in optically pumped graphene structures, http://arxiv.org/abs/1011.0238v1
15. Ratinac K., W. Yang, S.P.Ringer and F. Braet, 2010. Toward Ubiquitous Environmental Gas Sensors—Capitalizing on the Promise of Graphene. Environ. Sci.technol., 44, 1167.
16. Potyrailo R.A., C. Surman, N. Nagraj, A. Burns, 2011. Materials and Transducers Toward Selective Wireless Gas Sensing. Chemical Rev., 111, 7315.
17. Cui Y., S.N. Kim, S.E. Jones, L.L. Wissler, R.R. Nail and M.C. McAilpine, 2010. Chemical Functionalization of Graphene Enabled by Phage Displayed Peptides. Nano Lett., 10, 4559.
18. Lu Y., B.R. Goldsmith, Kybert and N.J. Johnson, 2010. DNA-decorated Graphene Chemical Sensors. A.T.C. Appl. Phys. Lett., 97, 083107
19. Pearce R., T. Iakimov, M. Andersson, L. Hultman, A. Lloyd Spetz and R. Yakimova, 2011. Epitaxially grown graphene based gas sensors for ultra sensitive NO2 detection. Sensors and Actuators B: Chemical, 155: 451-455.
20. Tzalenchuk A., S. Lara-Avila, A. Kalaboukhov, S. Paolillo, M. Syvajarvi, R. Yakimova, O. Kazakova, T.J.B.M. Janssen, V. Fal'ko and S. Kubatkin, 2010. Towards a quantum resistance standard based on epitaxial grapheme. Nature Nanotechnology, 5: 186-189.

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