Overview of the graphene film technologies

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Abstract. This work`s objective is review of contemporary literature on of the graphene film technology based on silicon carbide, comparison its advantages and disadvantages with other graphene technologies, definition of the optimality conditions and growth modes, and definition of the substrate parameters to produce the graphene with high structural perfection. The graphene interest is provided, first of all, by the graphene unique physical and mechanical properties like high thermal conductivity and electrical conductivity, high mobility of charge carriers, high elasticity, Hall quantum effect, band gap adjustability etc. The mentioned properties are very attractive in the context of the material possible application as a base for nano-electronics. The literature data review has shown that the silicon carbide thermal decomposition technique can be used in commercial production of high quality graphene layers. At the same time, the optimality parameters are: temperature ~ 2000^0C, argon atmosphere, silicon carbide oriented surface (0001). The substrate polytype is not of great importance.
[Bulat P.V., Lebedev S.P. **Overview of the graphene film technologies.** *Life Sci J* 2014;11(7s):198-202] (ISSN:1097-8135). http://www.lifesciencesite.com. 39

Keywords: graphene, silicon carbide, epitaxial growth, polytype, graphitization

Introduction

Graphene has the unique physical-mechanical properties: high thermal conductivity and electrical conductivity, high charge carrier`s mobility, high elasticity, Hall quantum effect, band gap adjustability etc. The mentioned properties are very attractive in the context of the material possible application as the base for nano-electronics. The graphene interest flared up after the publication of K.S. Novosyolov, A.K.Geim and others [1] where they demonstrate the graphene flake availability by means of micro-mechanical splitting of 3D crystalline graphite (fig.1).

The graphite micro-mechanical splitting is the first technique for the graphene monolayer experimental production. The principal is in graphene sheet release from crystal graphite with the help of adhesive film. In this case a number of graphene flakes with different quantity of layers (one monolayer to a hundred layers) appear. The main disadvantage of this technique is a few monolayer flakes of graphene among the general number of flakes, and their irregular form (fig.2). Therefore, this can be applied only for experimental study of the graphene physical and transfer properties. Later, a technique of the graphite ultrasonic splitting has been developed.

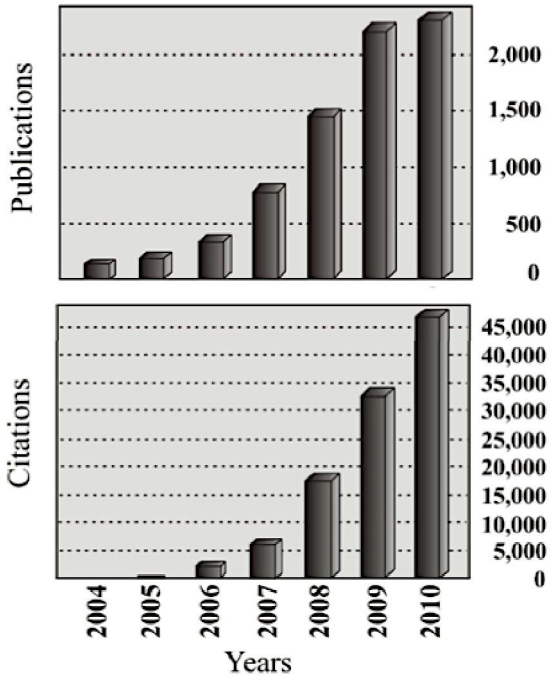

Fig.1. The graphene publications growth after the A. Geim and K. Novosyolov`s group produced the graphene first specimens

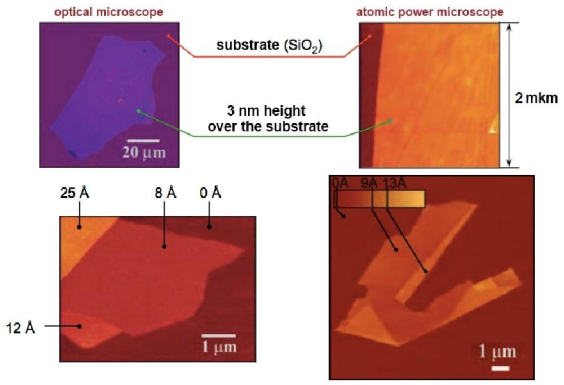

Fig. 2. Form of graphene flakes produced by the micro-mechanical splitting

For the layers number determination, flakes are transferred onto the silicone plate coated with 300 mcm SiO2, then, by means of an atomic power microscope and a spectrometer (Raman scattering), the layers number in the graphene flakes is identified, and monolayer flakes are separated for further study.

Lab methods of graphene production

The graphite liquid-phase splitting. This method, like the previous one, is based on the graphene separation from crystal graphite. However, chemical intercalation (graphite intercalation compounds) is used instead of scotch tape [2]. Molecules of the intercalating substance penetrate into the space between the graphite layers which results in the distance increase and attenuation of links between adjacent graphene layers (fig.3). Thermodynamically such a possibility is provided by higher energy of interaction of intercalating molecules and the graphene sheet surface as compared with graphene adjacent layers interaction. Further splitting of graphite into graphene sheets can be conducted by different methods: ultrasonic treatment, temperature treatment or mechanical flaking off.

The technique disadvantages are small sizes of individual graphene sheets and underevaporation of the intercalating substance after graphene sheets splitting: remains appeared as polyatomic layers bound together.

Technique of chemical vapor deposition (CVD). The technique is based on decomposability of hydrocarbon gas on the substrate surface with formation of carbon nanostructures. This technique is used not only for graphene production, but other carbon forms, for example, carbon nanotubes [3]. In general, metal is used for the graphene growth substrate, for example, nickel foil [4] (fig.4) or copper foil [5].

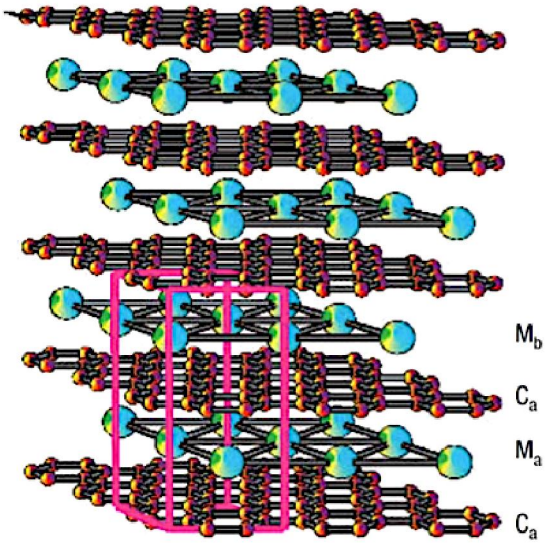

Fig.3. Intercalating substance molecules penetrate into the graphite layers space

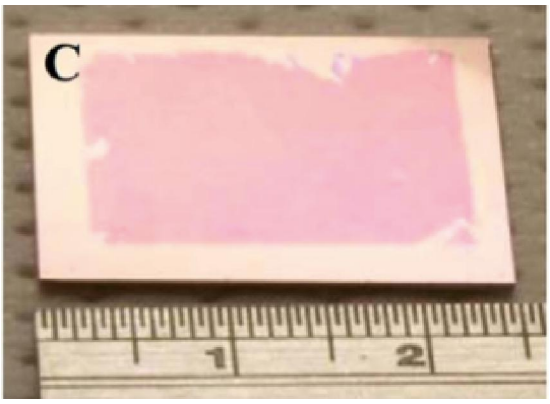

Fig.4. Ni foil CVD

In theory, this technique allows to receive graphene films by large area for different application. The CVD technique with following transfer of graphene from the metal foil onto polymeric insulating film is the most perspective for creation of different touch-sensitive screens, including flexible ones.

Graphene epitaxial growth on the metal surface. As opposed to the CVD method, gas is not used here as a carbon source. There is temperature growing dependence of carbon solution in transition metal in the technique bottom [6]. At high temperature, when solubility is high, the metal becomes saturated with carbon. Further slow cooling of metal results in carbon solubility decrease, which leads to excess carbon deposition on the metal

surface, and the surface gets covered with graphene islands.

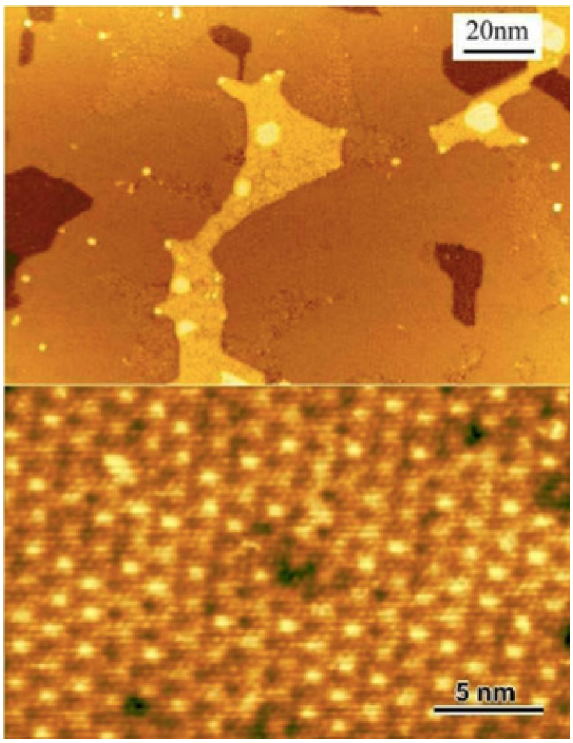

Fig.5. Graphene islands on the metal surface in case of graphene epitaxial technique

Graphene production under the silicon carbide thermal decomposition technique

The silicon carbide thermal decomposition technique [7] is based on nonstoichiometric evaporation of silicon components from the silicon carbide mono-crystal surface (SiC) and formation of the graphene film of residual carbon atoms (fig.6).

For this technique realization the SiC substrate should be heated up to high temperature (>1400°C). We know that when silicon carbide (SiC) heating in vacuum, silicon (Si) components nonstoichiometrically evaporates from the crystal surface and a carbon film appears. This fact was discovered long before discovery of a number of nanocarbon forms. E.g., the work [8] (the middle 60s) demonstrates the results of study of the silicon carbide crystal heated in vacuum up to o 2280°C under the roentgen diffraction technique. The author showed that on the SiC surface a pseudomorphic carbon film forms. For many years the silicon carbide surface graphitization phenomenon is considered negative in technology of SiC devices as the carbon film caused leakage current which considerably worsened the semiconductor operation.

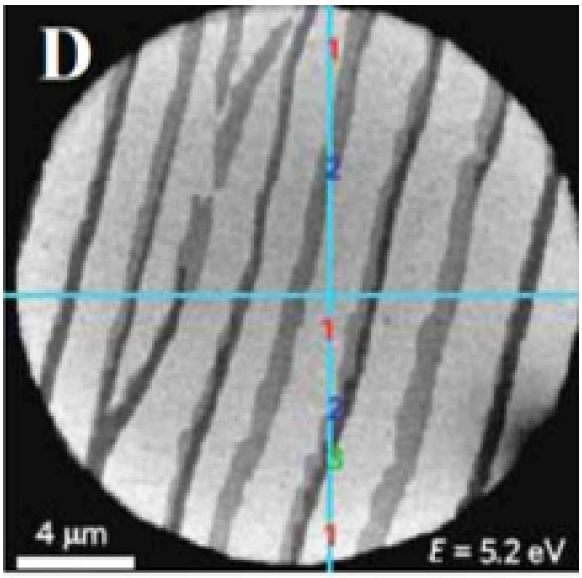

Fig. 6. Formation of graphene films on the silicon carbide surface

However, after a number of nanocarbon forms (nanotubes, fullerenes etc.) have been discovered, an idea of new carbon forms on silicon carbide by means of controlled thermal decomposition of the crystal surface in vacuum put forward. In works [9-10] the authors demonstrated availability of carbon nanotubes by diameter 3-5 nm and length about 0.25 mcm at heating on the SiC substrate C-edge up to temperature 1700°C during 30 minutes in vacuum (10-4 torr). In case of Si (0001)-edge at the same conditions 17 graphite sheets formed.

The main advantage of the silicon carbide thermal decomposition technique is value of the graphene grown which is limited with dimensions of the initial SiC substrate. Today, 6 inch (150mm) SiC substrates are commercially available. Another advantage of SiC is the fact that clear silicon carbide is actual dielectric with high resistance, therefore there is no need to transfer graphene onto dielectric substrate for transfer property research, therefore production of graphene on silicon carbide is prospective for creation of fast graphene transistors and gas sensors.

Comparison of different techniques of graphene production on SiC substrates

After the first experimental production of the monolayer graphene [1], the study was focused on production of the single-layer graphene film on SiC surface, and also on effects and phenomena both in graphene itself and in the system graphene/SiC. For today, a number of articles about the technology of graphene on different silicon carbide polytypes have

been published. For example, in the article [11] the process of thermal decomposition of SiC silicon edge of polytype 4H is described. Just before the process, the substrate was etched in the hydrogen atmosphere at temperature 1600°C. This operation removes from the substrate surface all scratches caused by polishing, and forms a regular stepping structure. After etching in hydrogen the sample was heated in some stages:

First stage – 11000C, annealing time- 6 minutes;

Second stage – 13200C and 8 minutes;

During the last stage the substrate was heated up to 1400-14400C and annealed at this temperature for 6-12 minutes. As a result, a graphene layer of 1-2 atomic layers formed on the Si-edge of the silicon carbide substrate.

In the article [12] the results of study of graphene grown on the silicon carbide surface of polytype 6H are presented. The authors investigated the graphitization of the substrate Si (0001) edge at temperature range 1350°C to 1500°C, the value of residual chamber pressure constituted 10-6 torr, and annealing time - 30 minutes. In result, with increase of the substrate annealing temperature the graphene film thickness increased too. If at temperature 1350°C the film thickness was 2 graphene monolayers, at temperature 1450°C the thickness increased up to 3 monolayers, and at 1500°C - up to 9 monolayers.

Matching the results received by the authors of [11] and [12], it is possible conclude that the difference in the structure of two polytypes 6H and 4H does not render essential influence on graphene formation, as the surface (0001) where the graphene was grown has identical structure for both polytypes. It is possible to suppose that in case of the SiC surface with crystalline attitude distinguishing from (0001), the graphene growth will differ.

Work [13] covers comparison of epitaxial graphene received on polar edges Si (0001) and C. At temperature 1320°C and residual pressure 10-8 torr a graphene film by thickness 2 monolayers formed on the Si-edge, while on C - edge the film thickness under the same conditions was 16 monolayers. The authors came to the conclusion that the graphene growth on Si-edge goes more slowly than on C - edge even at higher temperature. Also the authors approve that on the Si-edge the graphene grows more uniformly on the substrate area, while on the C- edge the growth has insular nature, therefore in different points of the graphene film there is wide scatter in thickness (film thickness in different points can differ by n 3-4 monolayers).

The described above results of the graphene growth were received in the vacuum chamber with high or ultrahigh vacuum. The alternative to vacuum can be argon which, due to its inertness, cannot chemically interact with both the silicon carbide substrate and components evaporating from its surface. However, controlling the argon pressure in the chamber, it is possible to change the pressure of vapors above the substrate, and control the graphene film growth rate.

The authors of the article [14] demonstrate that use of the argon atmosphere allows to receive graphene film on the Si-edge by thickness 1 and 2 monolayers, in this case the sizes of individual graphene sheets exceed 50 mcm^2 which is much more than in case of vacuum usage. The argon pressure in the chamber is 1 atm. which allows to increase the graphene growth temperature up to 2000°C. At temperature rise from 1400°C (vacuum) up to 2000°C (argon) carbon atom mobility increases on the substrate surface, and speed of silicon component sublimating on the SiC surface. On the other hand, the argon atmosphere prevents fast decomposition of the substrate surface. So, at high temperature atoms on the SiC surface have diffusion large length which promotes formation of broad terraces with monolayer graphene coating. In this case the argon atmosphere prevents formation of excess amount of carbon atoms on the surface which would result in increase of the graphene film thickness.

Conclusion

The work considers the basic techniques of the graphene production. It shows that technology of graphene film on the SiC substrates is one of most prospective for commercial production of graphene and its application in electronics. Different alternatives of the technology realization both in the vacuum and in the argon environment are reviewed.

Summary

It follows from the introduced material that the technique of thermal decomposition of silicon carbide can be used for receiving quality graphene layers. The technique has a number of advantages:

1. Technology of large sized graphene. The graphene film size is limited only to the sizes of SiC crystal. Today, the substrates by dia up to 6 inch (150 mm) are available.

2. Technology of the graphene grown on the silicon carbide insulating substrates, that is necessary for exception of influence of the substrate conductivity onto the performances graphene instruments.

3. The modern silicon carbide substrates have high structural perfection and low dislocation density which positively influences the graphene film quality.

According to the literature data, the optimal technological conditions of the graphene growth on silicon carbide are: temperature ~ 2000°C, argon atmosphere, oriented silicon carbide surface (0001). The substrate polytype isnot of great importance.

Acknowledgements

This article was prepared as part of the "1000 laboratories" program with the support of Saint-Petersburg National Research University of Information Technologies, Mechanics and Optics (University ITMO).

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5/1/2014