

OBTAINING OF GRAPHENE BY CHEMICAL VAPOR DEPOSITION

*H.L. Margaryan, N.H. Hakobyan, V.K. Abrahamyan, H.S. Chilingaryan,
Arpi S. Dilanchian Gharghani*

Yerevan State University, e-mail: marhakob@ysu.am

Introduction

The discovery of graphene has opened a new and very promising area of new physics and potential applications [1, 2]. Graphene, a monolayer of carbon atoms arranged in a honeycomb structure, is a unique material with outstanding properties: high optical transmittance, exceptional electronic transport, outstanding mechanical strength, and chemical stability. The striking electrical [3], mechanical [4, 5] and chemical [6, 7] properties of graphene make it suitable for use in flexible and transparent optoelectronics [8-10], biological sensors, energy storage conversion devices and etc. However, efforts to make transparent conducting films from graphene have been hampered by the lack of efficient methods for synthesis, transfer and doping of graphene at the scale and quality required for applications. Theoretical studies of graphene have begun long before obtaining the real samples. In the 30-40's on the past century the calculations showed that a free two-dimensional film should be thermodynamically unstable. For this reason monolayer structures were obtained only on the surface of bulk materials. The first steps for making single carbon layers were made in the 60-70's., using colloidal solutions of graphite oxide [11] and using methods of chemical vapor deposition of hydrocarbons on metal substrates [12] or on their carbides [13]. Another method showed that the high-temperature treatment of silicon carbide with silicon evaporation leads to the epitaxial growth of a single-layer carbon film [14, 15]. However, in all the works listed above, the films with the thickness of no less than 20-30 layers were obtained, which in their essence were not graphene.

A new stage of graphene development began with obtaining of single-layer and two-layer samples in 2004 [16], when the scientists, by multiple using of an adhesive tape, separated a monolayer of graphene from the bulk graphite and transferred it to the silicon substrate with oxide of 300 nm thickness. After demonstration of the unique electronic properties of graphene in these works, a rapid development of research of this material and the development of new methods for its production began.

Methods for obtaining graphene

The method of obtaining graphene is divided into several categories: detached graphene [16, 17, 18]; chemical graphene [19-21]; epitaxial graphene on metals [22-27] or on SiC [28-30]; chemical vapor deposition (CVD) graphene on nickel [31, 32] or on copper [33-36]. In order to obtain detached graphene from a plate of bulk well-oriented pyrolytic graphite by means of an adhesive tape multiple using, it is possible to separate the film into a single monolayer, which can be transferred to another substrate. The undisputed advantage of this method today is the obtaining of a graphene monolayer of the highest quality. Such samples are ideal for conducting experiments for electronic properties study, measurement of its conductivity or creation of prototypes based on graphene. The only and very significant drawback of this method is its inability to use it on production scale. Chemically graphene is obtained either by restoration of graphite oxide or by liquid-phase stratification of graphite. In the first case, a highly disordered material is obtained, which is far from its pure graphene properties. Liquid phase stratification of graphite, prolonged ultrasonic treatment and fine graphite centrifugation in the presence of a surface-active substance leads to the suspension formation containing not only single-layer graphene flakes, but also curved sheets and two-layer or multilayer graphene samples. When graphene is grown epitaxially on the metal surface (ruthenium, iridium, platinum, palladium, nickel, etc.) at a temperature exceeding 1000 °C, the metal saturates as a result of the chemical deposition of carbon from the gas phase. Further, in high or ultrahigh vacuum, when the substrate temperature decreases, the solubility of carbon in metal significantly decreases, and due to the thermal compression of crystal grating,

carbon appears on the surface, forming graphene domains of large area. The given method allows forming extremely thin and large-scale samples containing one or two layers, and having dimensions of highly oriented clusters up to 200 μm . On the other hand, graphene formed on the surface of the metal substrate cannot be transferred to any other substrate without damaging the metal. The fourth method is chemical vapor deposition (CVD). At 900 °C, a graphite film with thickness of ~ 400 Å is formed on metal substrate, the formation mechanism of which is quite simple. In a mixture of carbon-containing gas, hydrogen and argon at various pressures, gas decomposition takes place during heating. Further, with increase in temperature starting from 650 °C, the carbon atoms are deposited on a nickel substrate and at temperatures above 800 °C they begin to diffuse into the volume of nickel. The heating stops at temperatures 950-1000 °C and then, when the sample is cooled to room temperature, the crystal grating of the metal (due to thermal compression) squeezes out carbon atoms to the surface where they form a graphite-like structure, since the grating constant of nickel is very close to the constant graphite grating. When selecting certain synthesis parameters, like the nickel foil thickness, the maximum synthesis temperature, the synthesis time and the cooling rate of the sample, it is possible to achieve the formation of a thin graphene film - up to obtaining a monolayer of graphene. The formation of a graphene film on the surface of copper polycrystalline substrate is different. Since the solubility of carbon in copper is about 1000 times less than in nickel, then after the decomposition of carbon-containing gas and the deposition of carbon on the copper surface, diffusion into volume does not occur. As the temperature of the copper substrate increases, both the probability of graphene film formation and the covered area increase. In this case, the formation of multilayer graphene sheets is impossible on copper, since copper is a catalyst in the deposition of carbon. When the graphene monolayer is coated with a copper surface, the formation of subsequent layers becomes very unlikely. Today this method is used for a large-scale production of graphene.

The device description and experiment

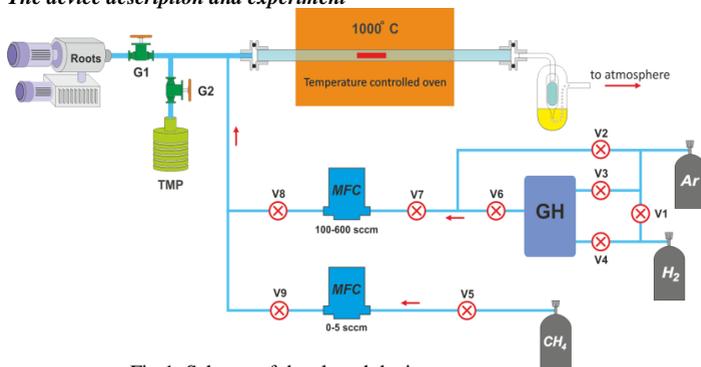


Fig.1. Scheme of developed device.

At the center of semiconductor devices and nanotechnologies of YSU an installation has been developed and assembled for graphene obtaining by the method of chemical vapor deposition from the gas phase. The scheme of the developed installation is shown in Fig.1. The installation consists of three main parts - a thermal reactor, a vacuum system and a gas distribution system. *The reactor* is a quartz tube of 22 mm diameter, placed in a heat furnace. In this case the furnace is installed on the base, which smoothly moves along the rails for withdrawal of the substrate- catalyst from the hot zone (synthesis zone) in order to cool the substrate after the end of the process. The temperature of the hot zone is controlled by FU-72 temperature controller in the range of 10-1200 °C with an accuracy of $\sim 0.5^\circ\text{C}$. At the outlet of the reactor, a bubbler is installed to exclude backflow from the atmosphere into the quartz tube and neutralize the exhausted gas mixture before

discharge to the atmosphere. *The vacuum system* consists of a Roots pump and a turbomolecular pump designed to clean the quartz tube and provide vacuum in the reactor. *The gas distribution system* consists of a tank for gases mixing with a reducer, gas pipes, a valve system and two programmable gas flow regulators.

The control of gas flow regulators and vacuum valves (V1-V9) is carried out by specially created software in the LabVIEW medium. A technological process for graphene obtaining on copper foil has been also developed. After chemical cleaning and electropolishing, the copper foil is placed in a quartz tube and dried in a stream of argon. At that the chamber is heated uniformly to a synthesis temperature of 1000 °C at a rate 20 °C/min in a stream of

argon at a flow rate 300 N/cm³/min. When the temperature reaches 1000 °C, the copper foil is annealed within 10 minutes. After the copper foil annealing, the process of graphene deposition begins, which lasts for 20 minutes. For this a 2% mixture of argon in hydrogen Ar:H₂ (80 sccm) and methane CH₄ (1sccm) is supplied into the chamber through MFCs. The heat anneals the copper increasing its domain size. The hydrogen catalyzes a reaction between methane and the surface of the Cu substrate, causing carbon atoms from the CH₄ to be deposited onto the surface of Cu through chemical adsorption. Then the furnace is abruptly moved along the rails in order to remove copper foil from the hot reaction zone. This keep the deposited carbon layer from aggregating into bulk graphite, and it crystallizes into a contiguous graphene layer on the surface of Cu. Once the graphene/copper foil has been removed from the furnace and cooled the graphene layer can be transferred an arbitrary substrate. As pilot samples graphene films on copper foil were obtained. The mono-layer graphene film was then transferred from the Cu foil to a pre-cleaned glass substrate by using a polymer support layer of polystyrene (PS, Mw 35k, 2% w/w in toluene) and an etchant acid (FeCl₃ aq, 0.5 M) to remove the Cu, as described elsewhere [37]. This was followed by a wash in a warm ethyl acetate bath to dissolve the supporting polymer layer. The obtained graphene was used as a transparent electrode in a liquid crystal cell. At that, for comparison with a hybrid LC cell, containing two sections with different transparent conductive layers - graphene and ITO, have been made. The work of the prepared cell as an optical valve was observed (Fig. 2).

The transmission spectra of the both sections have measured in the visible range (Fig.3).

As it seen from the figure, the cell with ITO electrodes is more transparent for the 400-500 nm wavelengths, and the cell with graphene electrodes - for wavelengths exceeding 800 nm. The transparency is the same for the 550-800 nm wavelengths range.

Conclusion

A device for graphene obtaining by CVD method is developed and assembled. A liquid crystal cell consisting of two sections with various transparent electrodes is made: graphene and ITO. The work of the obtained cell as an optical valve is shown, both sections of the cell function identically. Graphene can be successfully used as a transparent electrode in optical elements based on LC. This work was supported by State Committee Science MES RA, in frame of the research project № SCS 15T-1C157.

References

1. K.S. Novosolov, A.K. Geim, *et al.* Nature, **438**, 197 (2005).
2. A.K. Geim and K.S. Novoselov. Nat. Mater., **6**, 183 (2007).
3. H.W. Kroto, J.R. Heath, S.C. O'Brien, R.F. Curl, R.E. Smalley. Nature, **318**, 162 (1985).

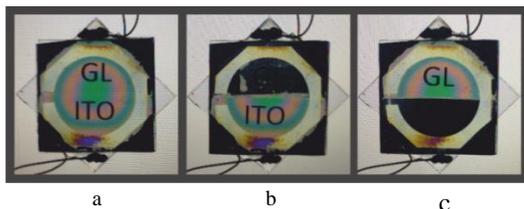


Fig. 2. Images of the graphene-ITO hybrid LC cell, obtained between crossed polarizers: voltage not applied (a), voltage applied to LC cell with graphene electrodes (b), voltage applied to LC cell with ITO

4. C. Lee, X. Wei, J.W. Kysar, & J. Hone. *Science*, **321**, 385 (2008).
5. J.S. Bunch, *et al.* *Nano Lett.*, **8**, 2458 (2008).
6. D.C. Elias, *et al.* *Science* **323**, 610 (2009).
7. X. Wang, *et al.* *Science* **324**, 768 (2009).
8. K.S. Kim, *et al.* *Nature* **457**, 706 (2009).
9. D.-H. Kim, *et al.* *Science* **320**, 507 (2008).
10. T. Sekitani, *et al.* *Science* **321**, 1468 (2008).
11. H.P. Boehm, *et al.* *Proc. of the Fifth Conf. on Carbon*, Pergamon Press, London, 1962, p.73.
12. M. Eizenberg, J.M. Blakely. *Surface Science* **82(1)**, 228 (1979).
13. T. Aizawa, *et al.* *Physical Review Letters* **64**, 768 (1990).
14. A.J. Van Bommel, J.E. Crombeen, A. Van Tooren. *Surface Science* **48(2)**, 463 (1975).
15. I. Forbeaux, J.-M. Themlin, J.-M. Debever. *Phys. Rev.*, **B 58**, 16396 (1998).
16. K.S. Novoselov, A.K. Geim, S.V. Morozov, *et al.* *Science* **306**, 666 (2004).
17. K.S. Novoselov, *et al.* *Proc. of the Nat. Acad. of Sci. of the USA* **102(30)**, 10451 (2005).
18. J.C. Meyer, *et al.* *Nature (London)* **446**, 60 (2007).
19. K.P. Loh, Q. Bao, P.K. Ang, J. Yang. *Journal of Mat. Chem.* **20**, 2277 (2010).
20. S. Park, R.S. Ruoff. *Nature Nanotechnology* **4**, 217 (2009).
21. O.C. Compton, S.T. Nguyen. *Small* **6**, 711 (2010).
22. Y. Pan, H. Zhang, D. Shi, *et al.* *Advanced Materials* **21**, 2777 (2009).
23. P.W. Sutter, J.-I. Flege, E.A. Sutter. *Nature Materials* **7**, 406 (2008).
24. T. N'Diaye, J. Coraux, *et al.* *New Journal of Physics* **10**, 043033 (2008).
25. P. Sutter, J.T. Sadowski, E. Sutter. *Physical Review B* **80**, 245411-1 (2009).
26. M. Gao, Y. Pan, *et al.* *Appl. Phys. Lett.*, **98**, 033101-1 (2011).
27. S.-Y. Kwon, C.V. Ciobanu, *et al.* *Nano Letters* **9(12)**, 3985 (2009).
28. E. Rollings, G. Gweon, *et al.* *J. of Phys. and Chem. of Solids* **67(9-10)**, 2172 (2006).
29. L.B. Biedermann, M.L. Bolen, *et al.* *Phys. Rev. B* **79**, 125411-1 (2009).
30. K.V. Emtsev, *et al.* *Nature Materials* **8**, 203 (2009).
31. Q. Yu, J. Lian, *et al.* *Appl. Phys. Lett.* **93**, 113103-1 (2008).
32. H. Cao, Q. Yu, *et al.* *J. of Appl. Phys.* **107**, 044310-1 (2010).
33. X. Li, W. Cai, *et al.* *Science* **324**, 1312 (2009).
34. X. Li, Y. Zhu, W. Cai, *et al.* *Nano Letters* **9(12)**, 4359 (2009).
35. S. Bae, H. Kim, *et al.* *Nature Nanotechnology* **5**, 574 (2010).
36. C. Mattevi, H. Kim, M. Chhowalla. *J. of Mat. Chem.*, **21**, 3324 (2011).
37. M.M. Qasim, *et al.* *Nanoscale*. **7**, 14114 (2015),

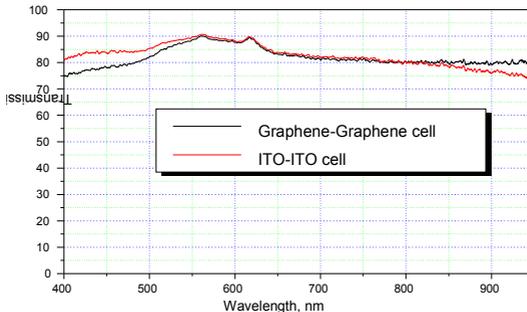


Fig.3. The transmission spectra of hybrid LC cell with graphene and ITO sections.