Advantage of few-layer graphene in comparison with graphene for applications

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The discovery of graphene opens way towards unique device architectures, functionalities and physical phenomena. The early period of investigation into the interesting properties of graphene has greatly extended the range of future applications of the material. Turning to applications surprisingly revealed the fact that few-layer graphene often demonstrates even more exiting properties than graphene itself. It can be argued that the discovery of few-layer graphene provides a basis for development of unique graphene-based devices for future electronics. For example, A.J. Hong [1] reported memory applications for graphene. Graphene flash memory has the potential to exceed the performance of current flash memory technology by utilizing intrinsic properties of graphene such as high density of states, high work function, and low dimensionality. Graphene (SLG) and few-layer graphene (FLG, thickness ~ 5 nm) flash memory devices formed on CVD large-area graphene sheets and integrated into a floating gate structure are compared in [1]. While SLG devices exhibit a memory window width of ~2 V using a program/erase voltage of ±7 V, FLG devices show a window width of ~ 6 V for the same program/erase voltage.

In our study [2] we have compared responses of SLG and FLG to gas absorption and have demonstrated extremely high gas sensing properties of p-type FLG flakes. The change in SLG resistivity due to adsorbed ammonia molecules is normally below several (~ 4 %) per cents (see, e.g. [3]). We have found that the current response of FLG to ammonia adsorption was strongly dependent on FLG thickness, and it exceeded the current response of SLG by 1 ÷ 7 orders of magnitude (Fig.1). A maximal response was found in FLG samples with thickness ~ 2 nm. FLG samples whose thickness was smaller than 3 nm demonstrated p-n conversion of flake conductivity. This finding suggested that our structures, at least those comprising less than ten graphene layers, were capable of showing a strong increase in resistance (10^7 times, switching effect) when exposed to ammonia ambient for moderate times. Samples with flake thicknesses ranging in the interval from 3 to 10 nm also exhibited pronounced responses to ammonia, showing from slightly above one order of magnitude to 25 % change in resistivity. No conversion to n-type conductivity was found in those samples. The high response of FLG flakes to ammonia adsorption can be understood within the framework of a model that implies the formation of multiple p-n-p junctions during ammonia absorption at the grain boundaries in polycrystalline graphene flakes considering the fact that the interlayer screening length in the material was ~1 nm [4]. Thus, polycrystalline FLG flakes may prove useful in gas sensor applications.

Growth of graphene is aimed at the development of graphene-based electronics. FLG has at least one layer that is not at the surface and not interacting with substrate, which is not susceptible to contamination and disorder due to processing [5]. Thus, grown graphene multilayers can be expected to be more important for application than monolayers. Moreover, a rich experience of graphite intercalation compounds can be used for creation of new hybrid materials or heterostuctures by means of intercalation of different substances into FLG. Intercalation ensures pure and two-side functionalization of graphene. A new interesting approach to creating a stable hybrid material with unexpected properties having considerable potential for future applications was developed in our group [6]. This approach is based on intercalation of the well-known polar solvent N-methylpyrrolidone (NMP) into few-layer graphene combined with heat treatment. Electrical properties of the new material proved to be dramatically different from those of graphene. We have included an anneal step into the fabrication process of our structures with the aim to stimulate the interaction of NMP with graphene sheets. Depending on process temperature, the obtained material could be produced with the following properties: a broad range of resistivity values (6 - 7 orders of magnitude, see Fig. 2) in combination with a high carrier mobility, tunable band-gap (from 0 up to 3 - 4 eV), and sp^2 or sp^3 hybridization of carbon atoms. An additional tool to manage with resistance of the hybrid material was found to be treatment of hybrid structures in hydrofluoric acid vapor. Such treatment during few minutes led to a strong decrease in resistivity of the hybrid material. For FLG structures, HF treatment leads to a decrease of flake resistivity by 10^2 ÷ 10^4 times and 10^7 x decrease of resistivity for graphene due to cleaning of the surfaces from NMP. So, HF treatment offers additional technological approach for managing with film properties. The revealed possibility to govern the surface conductivity by means of HF treatment gives us the way to monitor the local properties of the new material, and to create structures of the 'graphene - atomically thin high-resistivity barrier' type, which offer an unique tool for 2D and 3D nanostructuring and for design of novel devices.

References

[1]. A.J. Hong, E.B. Song, H.S. Yu, M.J. Allen, J. Kim, J.D. Fowler, J.K. Wassei, Y. Park, Y. Wang, J. Zou, R.B. Kaner, B.H. Weiller, K.L. Wang, ACS Nano, **10** (2011) 7812.

[2]. I. Antonova, S. Mutilin, V. Seleznev, R. Soots, V. Volodin, V. Prinz, Nanotechnology, **22** (2011) 285502.

[3]. F. Shedin, A.K. Geim, S.V. Morozov, E.W. Hill, P. Blake, M.I. Katsnelson, K.S. Novoselov, Nature Mat., **6** (2007) 652.

[4]. Y. Sui, J. Appenzeller, Nano Lett., 9 (2009) 2973.

[5]. W.A. de Heer, MRS Bulletin, **36** (2011) 632.

[6]. I.V.Antonova, I.A.Kotin, R.A.Soots, V.A.Volodin, V.Ya.Prinz, in press.

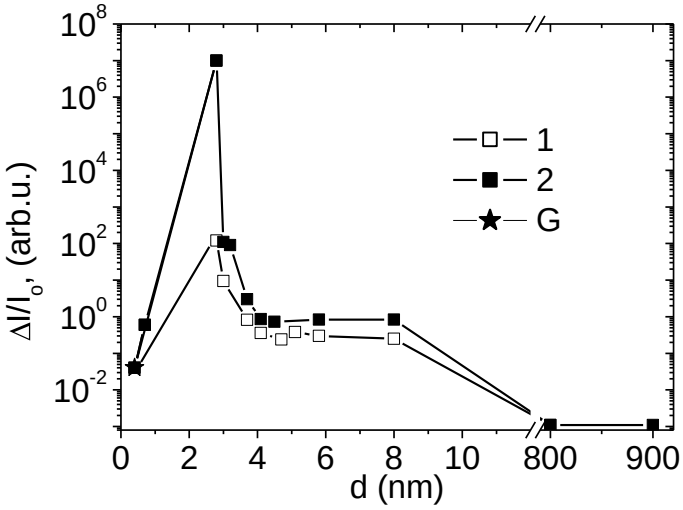

Figure 1. *Change in the current flowing through few-layer graphene flakes under NH_3 absorption as a function of flake thickness for two ammonia sources, 1 and 2, used to organize the gaseous air/ammonia ambient in the present study. Source 2 was an ammonia source more intense in comparison with source 1. The point G indicates the 4-% response of graphene to ammonia adsorption known from Ref. [3].*

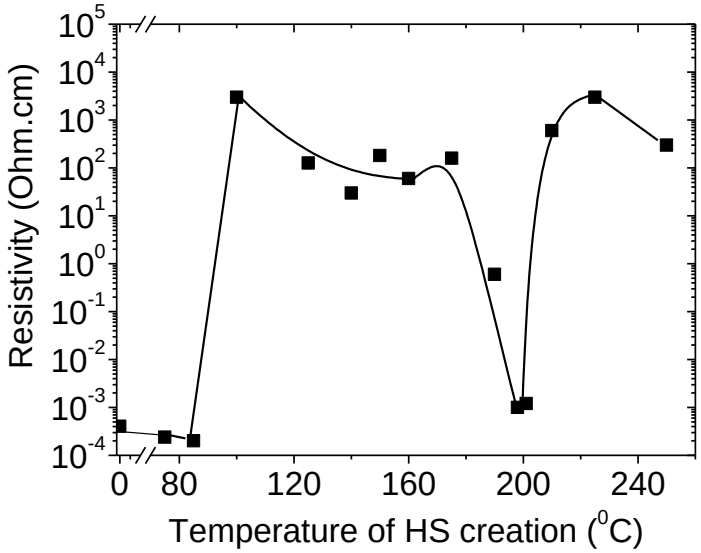

Figure 2. *Resistivity as a function of temperature at which the hybrid structures (HS) were fabricated. The resistivity of the reference FLG is indicated in Fig. 2 as a point at zero temperature.*