Gas- and bio-sensors based of graphene, produced by thermal destruction of SiC substrates

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The discovery of the ability of carbon to form a 2D modification (graphene) has resulted in an explosive rise in the number of publications concerned with the properties of this material and its possible application in electronics. It is known that, being a 2D material, graphene possesses a unique set of electrical and physical properties:
- high mobility of carriers in combination with their low concentration;
- maximum possible area-to-volume ratio;
- low noise level.

These properties combined result in that adsorption of a minimum amount of impurity on the surface of graphene can noticeably change its overall conductivity. Thus, graphene is a rather promising material for fabrication of various kinds of sensors.

It was shown in [1] that graphene is capable of sensing even the adsorption of a single molecule. Depending on their charge and on the conductivity type of the graphene film, added gas molecules behave as donors or acceptors. That is they change the concentration of mobile carriers. Adsorbed molecules also create additional scattering centers and change the carrier mobility. As a result, the resistance of a film either decreases, or increases, depending on the type of an adsorbed molecule [2, 3].

The graphene films used in the present study were grown on semi-insulating substrates of 6H-SiC by thermal decomposition of SiC at a temperature of ~1700ºC. Prior to growth of graphene, the substrate was etched at 1600ºC in the atmosphere of hydrogen to remove from the surface its defective layer. Results of measurements by Auger and Raman spectroscopies confirmed the presence of single-layer graphene on the surface of silicon carbide.

The sensor structure was formed on a graphene film by laser photolithography with an AZ5214 photoresist. Excess amounts of graphene were removed from the substrate surface by etching in oxygen-argon plasma. Ti/Au (5/50 nm) ohmic contacts were fabricated by lift-off photolithography after the metals were deposited onto the photoresist surface by electron-beam evaporation. The sensor chip was fixed on a holder together with two Pt100 resistors. One of these was used to measure temperature, and the other served as heater.

Relative measurements of the resistance of the graphene-based sensor were made in the presence of NO_2 in the gas mixture (gas supply periods are designated by light gray bands) at 20ºC. Because the NO_2 desorption rate at room temperature is very low, the sensor was annealed at 110ºC after each exposure in order to return it to the initial state. The sensors developed in the study demonstrated sensitivity to the NO_2 concentration at a level of 1--0.01 ppb.

Results are also presented, obtained in the development and testing of a graphene-based sensor for detection of protein molecules. The sensor was fabricated by the technology previously developed for the gas sensor. The working capacity of the biosensor was tested with an immunochemical system constituted by fluorescein and monoclonal antibodies (mAbs) binding this dye. The antibodies were attached to the graphene surface via amino groups formed by a number of electrochemical reactions. The biosensor was placed in a buffer borate solution to which fluorescein molecules were added. The attachment of fluorescein molecules to the antibodies situated on the graphene surface changed the total resistance of the graphene film. It was found that the sensor is sensitive to a fluorescein concentration at the level of 1-10 ng/mL and to a concentration of conjugate of bovine serum albumin with fluorescein on the order of 1-5 ng/mL. It is shown that the device is highly promising for early diagnoses of various diseases.

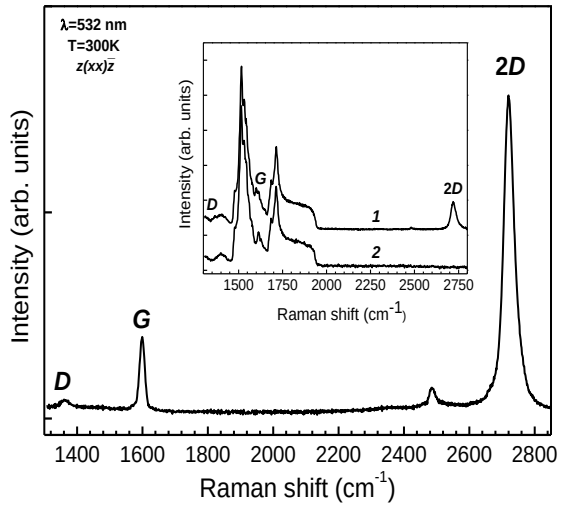

Fig. 1**.** Typical Raman spectrum of a graphene film grown on a 6H-SiC substrate. The inset shows the spectrum of the graphene /6H-SiC structure (1) and that of the 6H-SiC substrate 6H-SiC (2).

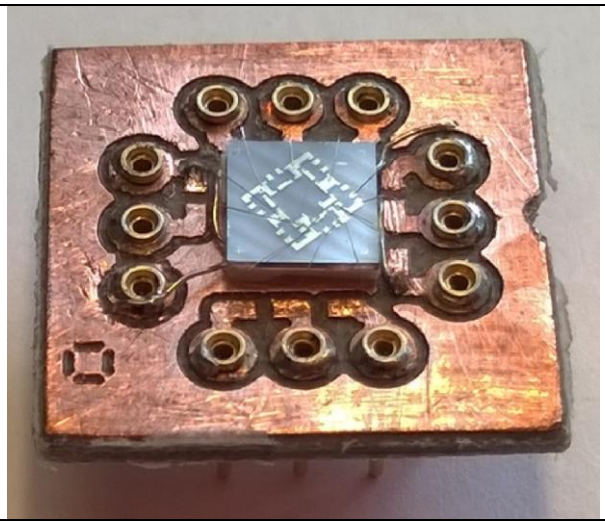

Fig. 2. Outward appearance of the sensor mounted in a case.

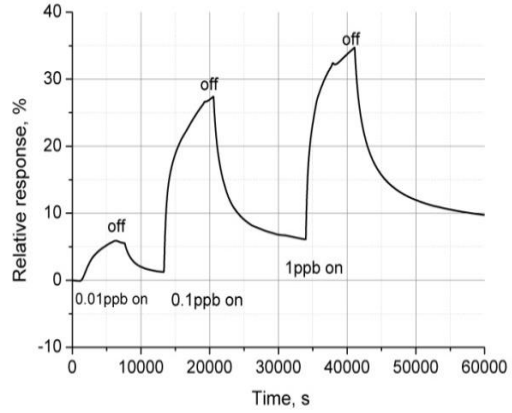

Fig. 3. Response to exposure to a gas mixture containing NO_2 gas at 100^{o}C for the graphene-based device.

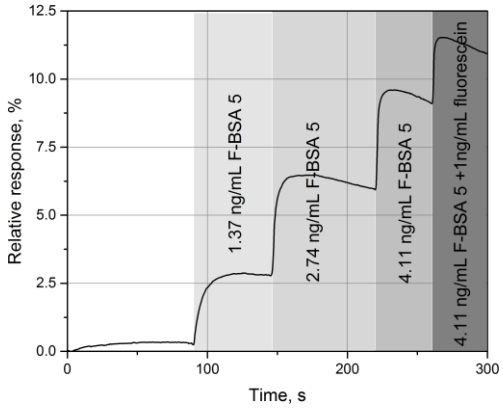

Fig. 4. Change in the sensor resistance brought in contact with solutions containing the concentrations of the BSA conjugate with fluorescein (F-BSA-5), specified in the plot, or a mixture of the conjugate and free fluorescein. The change in resistance in % is plotted along the ordinate axis, and the time of contact with the solutions (s), along the abscissa axis.

[1] F.Schedin, A.K.Geim, S.V.Morozov, E.W.Hill, P.Blake, M.I.Katsnelson, and K.S.Novoselov.// Nature materials. 2007. Vol. 6 P. 652-655.
[2] R. Pearce, T. Iakimov, M. Anderson, L. Hultman, A. Lloid Spetz, R. Yakimova// Sensors and Actuators B 155, pp. 451–455, 2011.
[3] S. Novikov, N. Lebedeva, and A. Satrapinski, Journal of Sensors, vol. 2015, Article ID 108581, 7 pages, 2015. doi:10.1155/2015/108581.