TUNABLE PROPERTIES OF A GRAPHENE-N-METHYLPYRROLIDONE MONOLAYER HYBRID STRUCTURES

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Chemical functionalization of graphene (or a few-layered graphene) is an advanced approach for creation of complementary materials with wide spectrum of an electronic properties. This method is used for band gap opening and managing with conductivity type, carrier concentration and mobility. The band gap has a central role in modern device physics and technology and governs the operation of semiconductor devices. A tunable band gap would be highly desirable because it would allow great flexibility in design and devices optimization. In present study we have used intercalation of N- methylpyrrolidone (NMP, C_5H_9NO) into a few-layered graphene with the aim to create a new graphene-based material with variable properties in controllable manner. Such approach as intercalation provides a pure and two-side functionalization of graphene. A choose of intercalation agent is based on well-known property of the NMP to penetrate between every graphene layers. As a result, we have created a new hybrid material with tunable properties.

Fabrication process of our hybrid structures (HS) includes the follows steps: (1) An electrostatic exfoliation of the few-layered graphene film with thickness about d $\sim 2-5$ nm and transfer it on the 300 nm SiO_2/Si substrate. (2) An intercalation of the NMP into the few-layered graphene flakes. (3) Annealing of the intercalated structures at temperature in the range of 125-250°C was the final operation which creates the hybrid structures. For convenience structures are marked according to temperature used for their creation (HS-125 - HS-250). Inserts in Fig. 1 demonstrate the schematic diagram and the optical micrograph one of our structures on SiO_2/Si substrate with two contacts. Ag alloy or evaporation of the Au is used for contacts.

Strong increase in resistivity (in 10^5-10^7 times) was revealed for hybrid material. Moreover, a sharp switching of resistivity for structures created at some temperatures was observed (see Table 1). Hybrid structures created in temperature ranges of T<200°C and T>200°C was founded to demonstrate strongly different properties. Two types of interaction between graphene and NMP are suggested for these structures. The first type of hybrid structures created at the temperatures of 125-175°C have high resistivity ($\sim 10^5$-10^6 Ohm), p-type conductivity, a strong increase in HS resistivity ($\sim 10^3$ times) with decrease in temperature from 300 to 77K and show an opening of the band gap ($\sim$3 eV for structures created at temperature of 150°C). We have presumed for these structures that bonds between NMP and graphene are formed through oxygen atoms. Alteration of the temperature of HS creation in this range causes some variation in resistance of the hybrid structures and band gap value

due to change in the number of NMP molecules interacted with graphene. Hybrid structures created at 200°C (boiling point of NMP) have properties similar to the initial few-layered graphene flake due to NMP evaporation from the interlayer spaces. The second type of hybrid structures graphene NMP corresponds to fabrication regime T>200°C. This structures are distinguish by appearance of the sp^3 hybridization of carbon atoms typically observed in the case of graphane formation. In our case sp^3 hybridization can be caused by such processes as polymerization or polycondensation with realizing of hydrogen atoms. The resistivity ρ of such structures is increased in 10^6-10^7 times in comparison with pristine graphene. Strong temperature dependence of the resistivity in the range of 77-300 K and band gap opening (∼3.5 eV) is also attributed to these structures.
The summary given above is illustrated in Fig.1a,b and Table 1. Figure 1a demonstrates Raman spectra for few HS samples annealed at different temperatures. Raman spectra reveals high quality of initial the few-layered graphene flakes and for HS-125 - HS-175 which follows from low intensity of D-line. The peak D at 1350 cm^{-1} is an indicator of intrinsic defects, or basal plane chemical reaction that disrupts the π-conjugation and converts sp^2 carbon atoms to sp^3 atom hybridization [1]. Raman spectra for structures created at T>200°C clearly demonstrates the hybridization of the carbon atoms from a sp^2 to a distorted sp^3 state.These statement is based on strong increase in D line Intensity, and appearance of additional peaks at 1625 and about 3000 cm^{-1}. Drain-source current I_{DS} versus gate voltage V_g curves for HS-250 are given in figure 1b. From the linear region of $I_{DS}(V_g)$ characteristics measured in transistor regime, the carrier (hole and electron) mobility was deduced (see Table 1). The carrier mobility is high enough for hybrid structures HS-150 and HS-250. $I_{DS}(V_g)$ characteristic for HS-250 given in Fig.1b is also clearly demonstrate formation of the band gap. Results of scanning tunneling spectroscopy measurements for HS-250 (and part of other our hybrid structures) are supported the conclusion about the band gap opening.

Sample	T, °C	ρ/ρ_o, arb.u.	μ_h cm^2/Vs	μ_e cm^2/Vs
Hybrid structures	125	$5x10^5$	11	88
	150	10^5	1360	3600
	175	$7x10^5$		
	200	$3x10^5$	-	-
	225	10^7	1	108
	250	10^6	920	2380

Table 1: Resistivity ρ extracted from $I_{ds}(V_{ds})$ characteristics of hybrid structures created at different temperatures. ρ_0 is the resistivity of pristine graphene. Hole and electron mobility μ_h and μ_e were extracted from $I_{ds}(V_g)$ characteristic measured in transistor configuration with use of the substrate as a gate electrode.

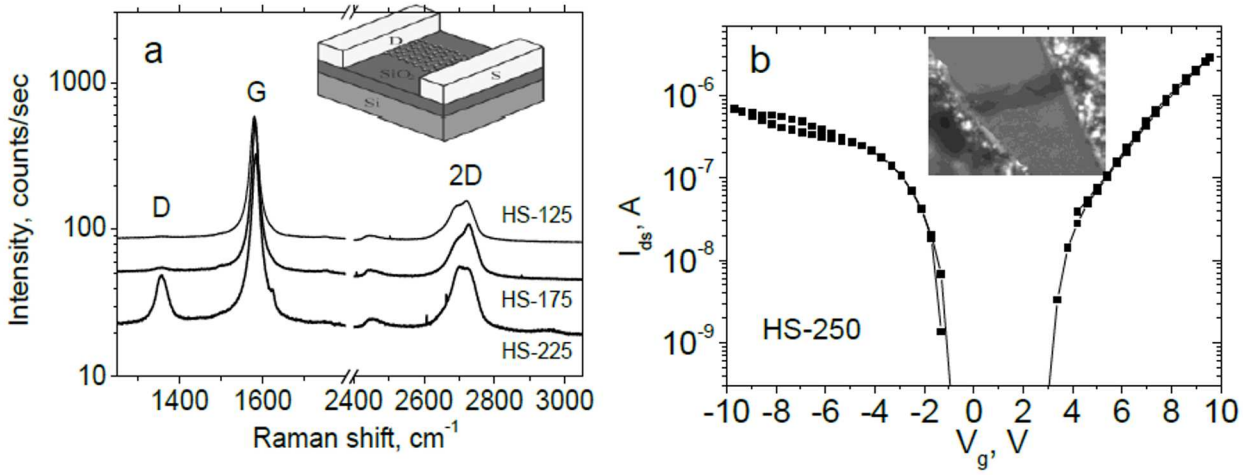

Figure 1: (a) Raman spectra of hybrid structures created at different temperatures. (b) Drain current at V_{ds}=150 mV as a function of the gate voltage for HS-250. Inserts give a schematic diagram and the optical micrograph one of HS on SiO_2/Si substrate with two contacts.

References

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