STUDY OF ELECTRICAL CONDUCTIVITY OF THERMALLY REDUCED GRAPHENE OXIDE

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Abstract. **Graphene oxide under study was obtained by a modified Hummers method. Samples were subjected to thermal reduction in a temperature range from 200° to 300°C in an atmosphere of argon and in vacuum. Results of measurements of volt-ampere characteristics of the samples in a temperature range from 80 to 300 K showed the presence of linear dependence of logarithm of current on a reciprocal temperature above 160-180 K. At temperatures below these values a power dependence of current on the temperature is observed. In this paper an assumption is made that both a Mott variable-range hopping (VRH) and the Efros-Shklovskii (ES-) VRH mechanism affect the electrical conductivity of graphene oxide in the range from 10 to 180 K. A contribution of each mechanism depends on conditions of carrying out the thermal reduction.**

Keywords: **materials for nanoelectronics, graphene oxide, thermal reduction, current-voltage curves, temperature dependence of resistance, mechanism of electrical conductivity, thermal activation mechanism, mechanism of the variable-range hopping.**

PACS: 53.039

Bibliography – 17 references *Recieved 7.09.2015*

RENSIT, 2015, 7(2):162-167 **DOI: 10.17725/rensit.2015.07.162**

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1. INTRODUCTION

A structure of graphene oxide (GO) is represented by randomly distributed on a surface of substrate small islets of graphene with sp^2 hybridized bonds surrounded by wide areas with sp^3 bonds functionalized by oxygen groups [1]. In the process of reduction there are removed functional oxygen groups (epoxy, hydroxyl, carbonyl, and carboxyl) and part of crystalline structure of graphene increases [1]. One of simple and effective ways of reduction of GO is heat treatment, as a result of which one succeeds in reducing the electrical resistance of GO by several orders of magnitude [1]. The reduced graphene oxide (RGO) is inferior to graphene in its electrical and thermal properties, but in spite of that it attracts interest of many researchers. This interest is due to capabilities of use of RGO as transparent electrodes, photodetectors, elements of power sources and others [2-6].

As it is shown in papers [7-11], in the range of temperatures below 200 K the dependence of electrical conductivity on the temperature in the RGO is in good agreement with the hopping mechanism of conductivity with the variable-range hopping. This type of transport of charge is described by an equation [12, 13]

$$R = R_0 \exp\left(\frac{T_0}{T}\right)^m, \quad (1)$$

where T is the temperature, T_0 is a characteristic temperature, m depends on a system dimension and takes on values 1/3 or 1/4 – two-dimensional [9, 10] and three-dimensional [11] structures, respectively. A similar dependence with a power $m = 1/2$ is observed for the Efros-Shklovskii mechanism [8, 11]. At higher temperatures the dependence of resistance has an activation

character and is described by an exponential dependence [7]

$$R = R_0 \exp\left(\frac{E_a}{k_B T}\right), \quad (2)$$

where E_a is the activation energy and κ_B is the Boltzmann constant.

When electronic devices on the basis of RGO are created, it is necessary to know influence of external factors on properties of material. One of main parameters of many devices is the electrical conductivity. The aim of this work was the study of effect of temperature on the electrical conductivity of thermally reduced GO obtained by the modified Hummers method.

2. MATERIALS AND METHODS

The studied graphene oxide was obtained by the modified Hummers method [14]. As a starting raw material to obtain a suspension of graphene oxide it was used graphite of company Sigma Aldrich. The suspensions of GO were subjected to ultrasonic treatment and centrifugation. As a result a homogeneous solution with average lateral dimensions of flakes of GO in a range of 0.4-0.8 μm was obtained. The aqueous solution of GO was deposited on a surface of SiO_2 with a thickness of 300 nm and was rolled by a metal rod to give uniformity in the thickness. The suspension of GO deposited in this way was evaporated at the room temperature during twenty-four hours. Silicon of *p*-type conductivity was a substrate for SiO_2. Heat treatments for the reduction were performed in a temperature range from 200° to 350°*C* of duration up to a few hours in an atmosphere of argon (**Table 1**). Measurements by methods of atomic force microscopy (AFM) and Raman spectroscopy (RS) were carried out with the help of a measuring complex "Ntegra Spectra" of company "NT-MDT".

Raman spectra of samples were measured using an excitation wavelength of 514 nm. Radiation power in a beam did not exceed 2-3 mW to prevent overheating of the sample. Also the surfaces of samples were studied with the help of scanning electron microscope of high resolution Jeol JSM 7800F. Measurements of electrical parameters were carried out on an apparatus ASEC-03 by a dual probe method in the temperature range from 80 K to 300 K. The current-voltage (IV) characteristics of GO were measured in a voltage range from –10 to +10 V after the reduction in the temperature range from 80 to 300 K. Before the reduction the samples showed dielectric properties with resistances greater than 10 GΩ. As contacts a silver paste was used.

Table 1

Processing conditions of sample

№ of sample	Treatment temperature, °C
OG-6	200
OG-1, OG-2, OG-3, OG-7	250
OG-4, OG-5	350

3. RESULTS

Fig. 1*a* shows a boundary of GO/SiO_2 measured by the method of electron microscopy for the sample OG-7. From the results of measurements

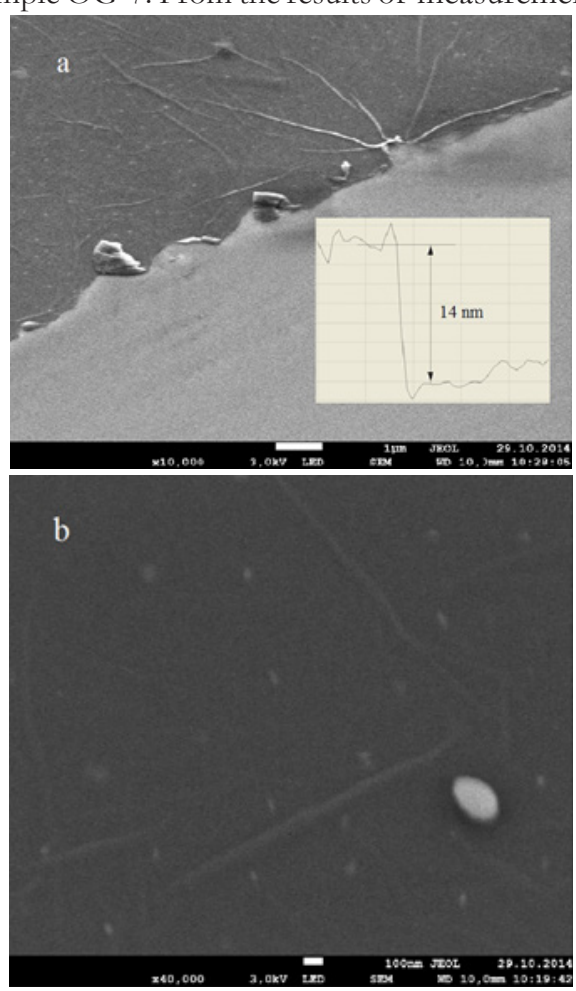

Fig. 1. *Image of boundary of GO/SiO_2 (a) and an enlarged image of the surface (b) of sample OG-7 after reduction obtained by scanning electron microscope. On inset of figure it is shown average value of height of step on boundary of GO/SiO_2 measured with AFM.*

it follows that GO is a film of relatively uniform thickness. Measurements of thickness of samples with the help of atomic force microscopy showed that the thickness of films of GO after the reduction decreases from 10-20 nm to 5-6 nm. As it is seen from the Fig. 1*b* a domain structure on the surface of GO does not become apparent. This means that sizes of graphene flakes do not exceed 10 nm.

In the Raman spectra of all studied samples there appear typical for RGO *D* and *G* peaks with maxima in the neighborhood of 1350 cm^{-1} and 1600 cm^{-1}, respectively. The Raman spectra of the sample OG-1 before and after the reduction are shown in **Fig. 2**. The peak *D* is due to disorder of crystal lattice and formation of sp^3 bonds, the peak *G* is due to the presence of sp^2 bonds of carbon in the lattice of graphene [15, 16]. Relationships of intensities of peaks I_D/I_G measured at different points of the sample before and after the reduction (at a temperature of 250°*C*), leads to a slight decrease in the average value of the ratio from 0.95 to 0.90. At the same time, a half width of peak increases by about 1.2 times.

The IV characteristics of sample OG-1 after the reduction with duration of 1 *h* are presented in a figure (**Fig. 3**). The current-voltage characteristics for all studied samples had a linear form, which indicates an ohmic nature of contacts. A difference in values of current at the temperatures of 80 and 300 K depends on the degree of reduction and is approximately two orders of magnitude. Sheet resistance of the samples ranged from a few to several tens of kΩ per square, depending on the conditions of reduction. On an inset of the figure it is shown the dependence of logarithm of resistance on the reciprocal temperature for sample OG-1. In the figure it is possible to mark out two parts. In the high temperature part of characteristic from the room temperature to 180-220 K a linear dependence is observed. At lower temperatures the dependence is different from the linear one.

4. DISCUSSION

With the help of formula (2) the activation energies E_a are calculated in the high temperature part of dependence of resistance on the temperature. The found values of activation energy are in a range of 0.032 to

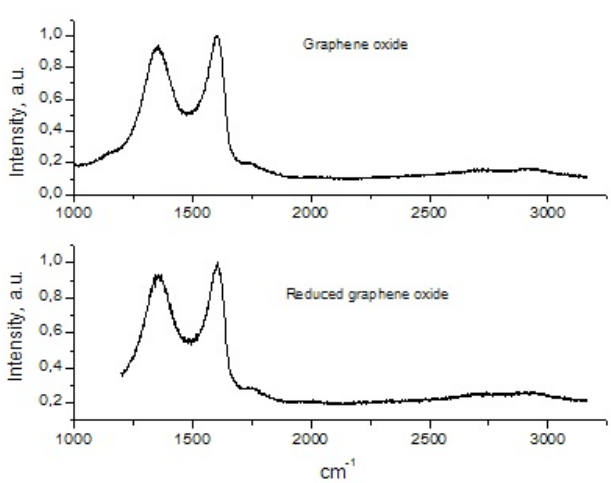

Fig. 2. *Raman spectra of GO for sample OG-1 before and after reduction in atmosphere of argon at temperature of 250°C with duration of 30 minutes.*

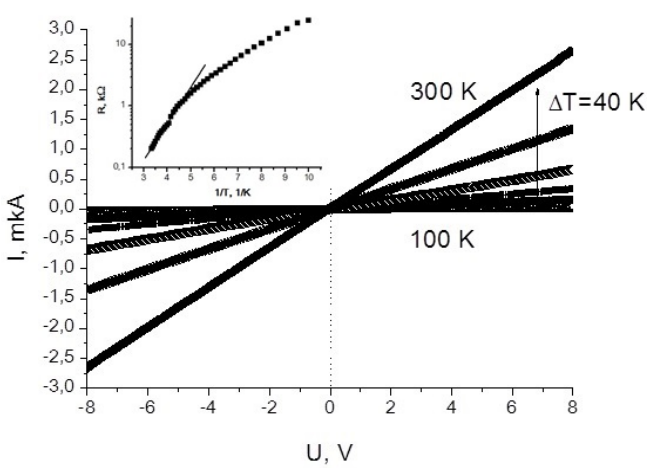

Fig. 3. *Current-voltage characteristics of sample OG-1 after reduction with duration of 90 minutes. On inset of figure there is dependence of logarithm of resistance on reciprocal temperature. Line corresponds to activation mechanism of electrical conductivity at temperatures above 200°C.*

0.12 eV (**Table 2**). As it can be seen from data of table 2, the value of energy E_a monotonically decreases with an increase of reduction time of GO (the samples OG-2 and OG-4). Also it is found that a temperature increase of reduction up to 350°*C* leads to a more rapid decrease of the activation energy to values of 0.03-0.04 eV (the samples OG-4, OG-5). The observed effects can be explained by transitions between states being far from the Fermi level, possibly interband transitions or states formed by functional groups of oxygen. As is known, recovery of the GO is accompanied by the departure of the various functional groups of oxygen, which can lead both to decrease the band gap [17], and the transformation of defect-impurity structure [1].

Low-temperature dependences of resistance on the temperature are different from the linear one (the inset of Fig. 3). To analyze a mechanism of conduction in this temperature range (ΔT) there are plotted the dependences of logarithm of resistance on T^{-m}, where m = 1/4, 1/3, and 1/2, in accordance with formula (1), and there are determined coefficients of linearity (b) of these dependencies. The obtained results are shown in Table 2. From an analysis of these data it follows that at temperatures of treatment of 200° and 250°*C* with an increase of time of reduction a transition happens from a dependence $R(T)$ with the degree 1/3 to a dependence with the degree 1/2. This transition corresponds to a change of the hopping mechanism of charge transport with a variable range hopping in the two-dimensional structures to the Efros-Shklovskii mechanism [12, 13]. At the temperature of reduction of 350°*C* already a half-hour heat treatment leads to the dependence with the degree 1/2. An estimate of characteristic temperature T_0 from formula (1) gives a value of 2300 K. T_0 is related with the localization length of charge states ξ with the help of expression [17]:

$$T_0 = \frac{2,8e^2}{4\pi\varepsilon\varepsilon_0 k_B \xi}, \qquad (3)$$

where ε_0 is the electric constant and ε is the permittivity of the material. For the graphene oxide ε is equal to 3.5 [8]. A calculation of the localization length ξ according to formula (3) gives a value from 4.3 to 6.1 nm for samples reduced at the temperature of 350°*C* and less than 2.5 nm at T = 250°*C*. These data agree with the data of Raman spectrum, in which a decrease of the ratio of intensities is observed, which indicates a decrease of number of edge defects caused by an increase of sizes of domains of graphene [16]. At the same time

Table 2.

Change of activation energy at temperatures above1800 K, change of coefficient of linearity b at different powers m in temperature range ΔT, characteristic Efros-Shklovskii temperature T0 and localization length of charge states ξ.

Sample	Activation energy E_a, eV	Time of reduction, h	linearity coefficient, b			ΔT, K	T_0, K	ξ, nm
			m = 1/4	m = 1/3	m = 1/2			
OG-1	0.12	1.5	0,99877	0,99893	0,99901	80-180	8913	1.5
OG-2	0.07	0.5	0,99893	0,99875	0,99824	80-150		
OG-2	0.06	1	0,99960	0,99960	0,99938	80-180		
OG-2	0.046	1.5	0,99902	0,99933	0,99975	90-180	5200	2.5
OG-3		0.5	0,99883	0,99875	0,99824	80-150		
OG-3		1.5	0,9996	0,9996	0,99836	80-180		
OG-4	0.04	0.5	0,99872	0,99899	0,99937	90-175	3100	4.3
OG-4	0.032	1	0,99894	0,99918	0,99952	100-175	2304	5.8
OG-5	0.045	0.5	0,99862	0,99898	0,99948	85-180	2206	6.1
OG-6	0.044	1	0,99879	0,99890	0,99877	80-200		

the width D of the line increases associated with an increase of disorder of lattice at the time of heat treatment [16].

5. CONCLUSION

Thus, it follows from the obtained results that the mechanism of conductivity in graphene oxide obtained by the chemical method and thermally reduced in the temperature range of 200°-350°C in the region of temperatures above 180 K is determined by the activation mechanism. And the activation energy depends on the degree of reduction, which is probably related to the decrease of the width of forbidden zone. In the temperature range of 100-180 K there are shown the hopping mechanism of conductivity with the variable length of hop in the two-dimensional structures and the Efros-Shklovskii mechanism in the samples with a higher degree of reduction (longer treatments and a higher temperature of reduction). For this case it was carried out an estimate of sizes of domains of graphene, which reach 6.1 nm during the reduction at T = 350°C and 2.5 nm at T = 250°C. The obtained results can be used to create the transparent electrodes, the photodetectors on the basis of RGO, the power sources, operating in the conditions of low temperatures.

ACNOLEGMENT

The work was performed according to the program of state task of the Ministry of education and science of the Russian Federation for higher educational institutions and scientific organizations in the sphere of scientific activity for 2014 (ST of the MES of the RF).

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