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REGULAR ARTICLE

Thermoresistive Properties of Graphite Films

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This work investigates the thermoresistive properties of graphite films made on different types of substrates. The study of the graphite films created by different methods: freehand drawing on paper using different types of graphite (including ordinary pencils), as well as vacuum deposition on InSe and SiO_2 substrates. The temperature dependence of the resistance of the graphite films in the range of 273÷380 K was measured, and the mechanisms of current flow were discussed. The experimental results demonstrate a decrease in resistance with increasing temperature for all structures of graphite films, with variations depending on the uniformity of the film surface and the types of graphite used. There are calculated the height of the barrier at the grain boundary, which plays an important role in determining the resistance of the films. It is concluded that both drawn and vacuum-deposited graphite films exhibit thermoresistive properties, and the resistance depends on the height of potential barriers in the polycrystalline structure. The experimental data are approximated within the framework of known theoretical models. The temperature coefficient of resistance is calculated. The obtained results are important for the development and calibration of thermistors in various electronic applications, offering an understanding of the resistance behaviour of graphite films under different temperature conditions.

Keywords: Graphite on paper, Thermistor, Temperature coefficient of resistance.

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1. INTRODUCTION

Thermistors are non-linear semiconductor resistors that differ in significant temperature dependence of their electrical resistance. This special nature of their response to temperature changes makes thermistors an important component of semiconductor devices that are widely used to solve various tasks of modern electronics.

Now, thermistors are made of various semiconductor materials. For this, doped germanium and silicon, silicon carbide, as well as III-V semiconductors and other materials are used. Such a diverse selection of materials allows optimizing the properties of thermistors, ensuring their effectiveness in a wide range of practical applications.

In recent years, flexible electronics based on various types of sensors: thermoresistive [1], piezoresistive [2], touch sensor [3], etc. have attracted considerable attention. To create prototypes of such flexible sensors, a simple and cheap technology of drawing on paper with conductive material is successfully used [4]. Among the various tools for creating conductive and piezoresistive traces on paper, a pencil containing graphite and clay turned out to be affordable and effective [2, 5]. The lead of a pencil (except for binders) consists of a large number of layers, which are formed by nano- and microparticles of graphite. The process of making conductive layers using a pencil consists in the mechanical exfoliation of graphite flakes on the rough porous surface of cellulose paper. The main advantages of this technology are low cost, variety of materials and ease of manufacture.

The paper [1] investigated the temperature dependence of graphite on paper (GOP), conducted an analysis of electrical conductivity mechanisms, and showed the possibility of using graphite traces on paper as sensors of temperature and air flow speed. Currently, prototypes of flexible temperature sensors based on graphite on paper [1], graphene in a polydimethylsiloxane matrix [6], polymer-graphite composite materials [7, 8] and many others have been fabricated.

The purpose of this work is investigation of thermoresistive properties of GOP obtained from different types of graphite and compare them with graphite structures obtained on other surfaces (in particular, InSe, SiO_2), as well as to analyze the temperature dependence of the resistance of the studied structures within the framework of known mechanisms of conductivity of graphite materials. We demonstrate that pencil traces can function as thermosensors, the conductivity of which depends on the ambient temperature.

2. EXPERIMENTAL

To created graphite on paper, we used a commercial pencil with a lead hardness of 6B grade, compressed

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thermally expanded graphite (TEG) and synthetic graphite (SG). According to [9], the content of graphite in the 6B pencil is 84 wt %, the rest is wax (5 wt %) and clay (10 wt %). The samples were drawn by hand on white office paper with a density of 80 g/cm². The size of the drawn GOP sample was 10 × 4 mm². Thin layers of graphite were also deposited on the surface of InSe and SiO_2 by vacuum deposition. Graphite powders with a dispersion of less than 100 μm were used for the research.

The growth of graphite films on the surface of InSe and SiO_2 crystals was carried out by the mechanism of van der Waals epitaxy. The use of this growth mechanism makes it possible to form heterostructures on substrates of different nature and with different types of crystal lattices of the deposited layer and substrate. Evaporation of graphite was carried out using electron beam irradiation of a graphite target. The target is a graphite electrode under a positive voltage of 1000÷2800 kV (the current, depending on the conditions, varied between 50 mA and 170 mA). The evaporation process was carried out in a vacuum of 10^{-4} Pa. As a result of the thermal radiation of the anode, the temperature of the substrates during deposition increased to 210÷250 °C in the first 10 minutes of the process. In the future, if the process is longer, the temperature reached 320 °C. By adjusting the sputtering modes of graphite layers, it is possible to obtain materials of different thicknesses and with different average crystallite size L.

Contacts on the surface of the films were applied using a conductive silver paste. The resistivity of the contacts was monitored by measuring the *I-V* characteristics along the films. The study of the temperature dependence of the resistance was carried out in the range of 273÷380 K. The electrical parameters were determined on the Solartron 1255 measuring complex. Visual control of the surface of the obtained graphite materials was carried out on an optical microscope with a 600-fold magnification.

3. RESULTS AND DISCUSSION

Examination of the surface of the graphite films with the help of an optical microscope showed the dependence of the surface uniformity of the structures on the technology of their preparation. The highest quality surface was obtained for the films deposited on the InSe substrate, and for the GOP that drawn with synthetic graphite.

The lead of a pencil consists of a large number of graphite particles bound together by auxiliary substances. Pencil traces on paper can be considered as thin polycrystalline graphite films, the average grain size of which can be 20÷490 nm [1, 10]. According to the Raman spectra obtained in the paper [11] for graphite nanostructures obtained by vacuum deposition on InSe substrate, the average grain size of carbon crystallites can be estimated [11]:

$$L = 2.4 \times 10^{-10} \times \lambda^4 \times (I_D/I_G)^{-1} \quad (1)$$

where λ is the wavelength of the radiation source (λ = 532 nm), I_D and I_G are the D and G band intensities. The calculated average grain size L is 20 nm.

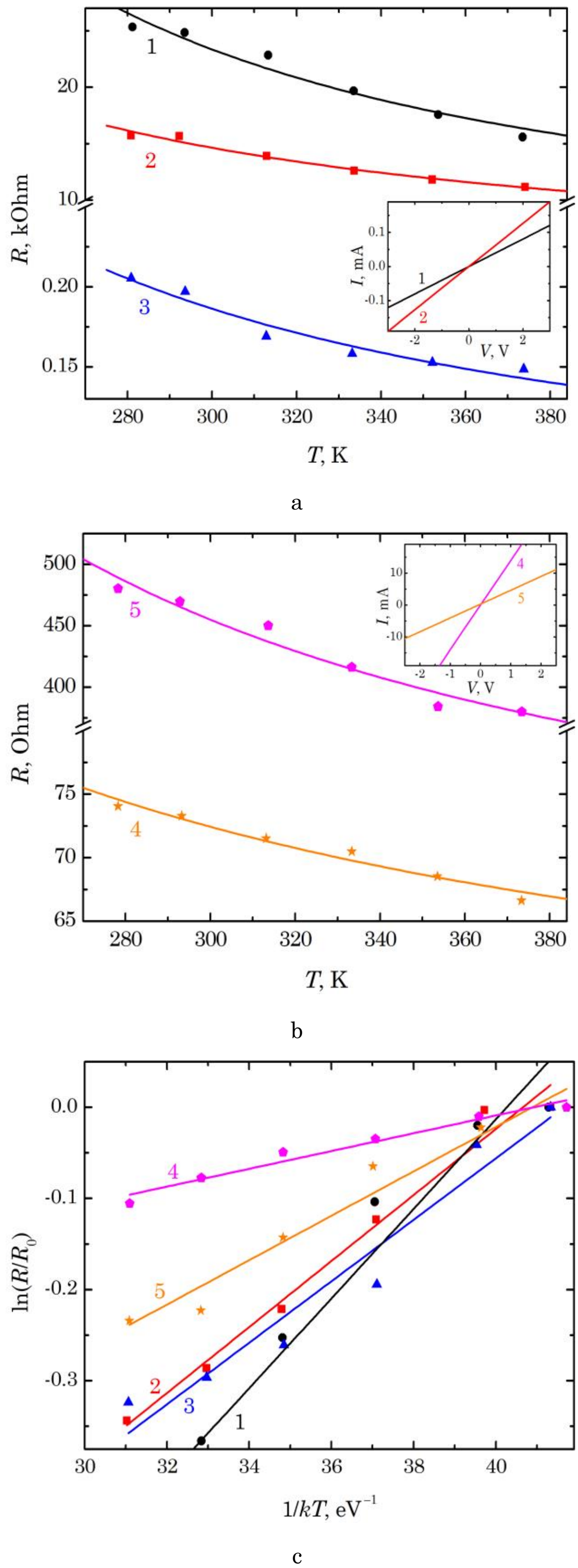

Fig. 1 – Temperature dependence of resistance (points are experimental data, curves are approximation by formula (2)): 1 – pencil drawing on paper, 2 – TEG drawing on papers, 3 – SG drawing on papers, 4 – vacuum deposition on InSe substrate, 5 – vacuum deposition on SiO_2 substrate

Quality control of the contacts to graphite structures was performed on the basis of *I-V* characteristics. The linear dependence of the *I-V* characteristics and symmetry relative to point 0 confirms the ohmic nature of the contacts (see inserts to Fig. 1a, b).

Fig. 1a shows the temperature dependence of the resistance of graphite films obtained by drawing on paper with different graphite: thermally expanded graphite, synthetic graphite, pencil of 6B. Fig. 1b shows similar graphs for films obtained by vacuum deposition of graphite on SiO_2 and InSe substrates. All structures are characterized by a decrease in resistance with increasing temperature. The change in resistance investigated temperature range is 28÷38 % for GOP, and 10÷21 % for solid substrates.

The resistance of polycrystalline graphite films consists of the resistance of individual crystallites and the resistance of their boundaries. The resistance of the grain boundaries significantly exceeds the resistance of the grains and the temperature dependences of the resistance can be approximated by an exponential dependence [1] (see Fig. 1a, b):

$$R \sim \exp(E_b/kT), \qquad (2)$$

where E_b is the height of the barriers formed at the grain boundaries, k is the Boltzmann constant.

The barrier height was determined from the slope of the dependence of $\ln(R/R_0)$ on $1/kT$ (see Fig. 1c). R_0 is the resistance at the minimum measurement temperature $T = 280$ K. The found values of E_b are given in the Table 1. It was found, that greater the uniformity of the film surface, that smaller the E_b.

Table 1 – The barrier height

	E_b, meV
Vacuum deposition on InSe substrate	10
Vacuum deposition on SiO_2 substrate	24
SG drawing on papers	35
TEG drawing on papers	36
Pencil drawing on paper	47

An important parameter of temperature sensors is the temperature coefficient of resistance α:

$$\alpha = 1/R \cdot (dR/dT) = -E_b/kT^2. \qquad (3)$$

Fig. 2 shows the results of theoretical calculations of α using formula (3) with E_b from Table 1.

For semiconductor thermistors $\alpha = -E_g/2kT^2$, where E_g is the band gap width. The temperature coefficient of resistance for semiconductors takes large negative values, in particular $\alpha(\mathrm{Si}) = -70 \times 10^{-3}$ K^{-1} ($T = 293$ K) [12]. The resistance of metals increases with a temperature, which is due to carrier scattering on phonons. This increase has a linear character and α has a positive value of the order of 10^{-3} K^{-1}, and for alloys it is much lower of the order of 10^{-5} K^{-1}.

Graphite is a semimetal, and its semiconducting properties are determined by the overlap of the valence band and the conduction band at the extrema of the Brillouin zone. The temperature dependence of the resistance has a semiconducting character and, as noted above, is determined by the barriers at the grain boundaries. The obtained values of α for the studied graphite materials at 300 K are in the range from $-1 \cdot 10^{-3}$ K^{-1} to $-6 \cdot 10^{-3}$ K^{-1} (see Fig. 2).

Usually, the Steinhart-Hart equation is used for calibrating of the thermistors:

$$1/T = a + b \cdot \ln(R) + c \cdot [\ln(R)]^3 \qquad (4)$$

Calculations of coefficients a, b, c for our materials show that c is very small and the third term in equation (4) can be neglected. Then only the first two terms remain, which leads to the following formula:

$$R = \exp[(1 - a \cdot T)/(b \cdot T)] \qquad (5)$$

The temperature dependences of $R(T)$ calculated according to (2) (see Fig. 2) and (5) completely coincide. Therefore, it makes no difference which of the formulas to use for calibrating thermistors made of our materials. The mean squared errors of fitting graphical dependences $R(T)$ by formulas (1), (5) are less than 4 %.

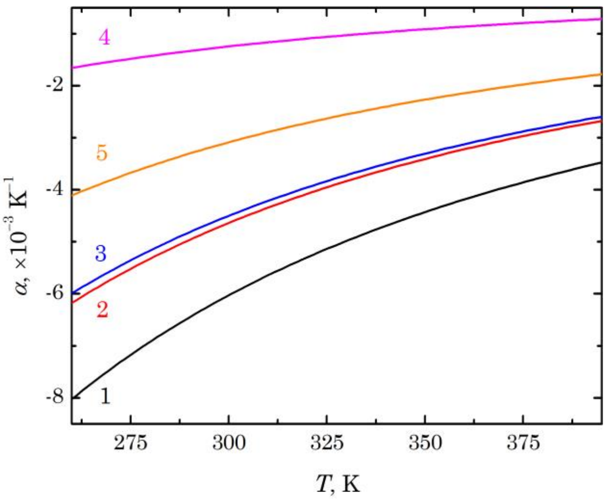

Fig. 2 – Temperature dependence of temperature coefficient of resistance: 1 – pencil drawing on paper, 2 – TEG drawing on papers, 3 – SG drawing on papers, 4 – vacuum deposition on InSe substrate, 5 – vacuum deposition on SiO_2 substrate

4. CONCLUSION

Graphite films were obtained by various methods: drawing on paper and vacuum deposition on InSe and SiO_2 substrates. Their thermoresistive properties were studied in the temperature range of 273÷380 K. It was shown that the resistance of the films decreases exponentially with increasing temperature. The resistance of the GOP is determined by the height of the potential barriers resulting from the polycrystalline structure of the films.

The temperature coefficient of resistance α was determined. For graphite films obtained by drawing on paper $\alpha \approx -(4.5 \div 6) \times 10^{-3}$ K^{-1}, and for films obtained by vacuum deposition on a solid surface (InSe, SiO_2) $\alpha \approx -(1 \div 3) \times 10^{-3}$ K^{-1} at room temperature.

The temperature dependences of resistance of graphite films were approximated based on the model of activation conductivity and using the Steinhart-Hart equation. Any of them can be used for calibration of the thermistors.

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Терморезистивні властивості графітових плівок

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В даній роботі досліджено терморезистивні властивості графітових плівок, виготовлених на різних типах підкладок. У дослідженні розглядаються графітові плівки, створені різними методами: малювання від руки на папері з використанням різних видів графіту (включаючи грифелі від звичайних олівців), а також вакуумне осадження на підкладки InSe і SiO_2. Проведено виміри температурної залежність опору отриманих графітових плівок в діапазоні 273÷380 К, обговорено механізми протікання струму. Експериментальні результати демонструють зменшення опору з підвищенням температури для всіх плівок, з варіаціями, що залежать від однорідності поверхні плівок і типів використаного графіту. У дослідженні розраховано висоту бар'єра на межі зерен, яка відіграє важливу роль у визначенні опору плівок. Зроблено висновок, що як намальовані, так і осаджені у вакуумі графітові плівки проявляють терморезистивні властивості, причому опір залежить від висоти потенціальних бар'єрів у полікристалічній структурі. Проведено апроксимацію експериментальних даних в рамках відомих теоретичних моделей. Розраховано температурний коефіцієнт опору. Отримані результати є важливими для розробки та калібрування терморезисторів у різних електронних додатках, пропонуючи розуміння поведінки опору графітових плівок за різних температурних умов.

Ключові слова: Графіт на папері, Терморезистор, Температурний коефіцієнт опору.