Influence of graphene stacks on the structure and conductivity of shungite carbon

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Abstract. The influence of graphene stacks on the formation of structural and electrical parameters of shungite carbon was determined. The spatial distribution map of graphene layers and stacks consisting of these layers was obtained by the STEM method. Statistical analysis of images of graphene stacks and the gaps between them was performed. Based on the data obtained, a simplified regular structure model is proposed, within the framework that allows one to quantitatively estimate the spatial dimensions of the carbon regions and describe the integral conductivity of shungite carbon.

1. Introduction

One of the most important tasks of modern electrical and radio engineering is the creation of shields that reliably block electromagnetic radiation from low to ultrahigh frequencies [1,2]. The natural material shungite [3-5] has a significant absorbing capacity in a wide frequency range - from a few megahertz to tens and hundreds of terahertz [6-10], and is a promising material for absorption. Large reserves of shungite deposits provide a low price, which is especially important for creating coatings of a large area.

Shungite is a rock with non-crystalline carbon [11]. The high shielding ability of shungite in a wide frequency range is due to the chaotic spatial distribution and the random length of the conducting regions. For this reason, for an electromagnetic wave of any length, conditions are found that ensure its significant interaction with the material. The dynamic absorption properties are similar to those for the granular structure and can be interpreted within the framework of the granular current model [12].

The shielding properties of an inhomogeneous material are determined by the spatial structure of the conductive matrix with non-conductive gaps. Understanding the conductive properties of the matrix is important. Studies of the structure of shungite are summarized in the work [11]. The structure of shungite carbon is complex, as a result of which there have been very few attempts to represent it in the form of various models [11]. At the nanoscale level, conductive formations in shungite have stacks consisting of a large number of flat or curved graphene layers, which are superimposed on each other in the form of stacks. Stacks can be grouped into more complex formations – globules and ribbons. The size of the stacks is the first nanometers, the stacks are oriented randomly in space. The conductivity anisotropy of
the stacks is due to the anisotropic properties of the conductivity of the graphene layer [13–14], but it is retained only within the stacks itself. The conductivity of the entire sample is generally isotropic.

To analyze such structures, the method of current tubes was proposed in [15], within the framework of which it is assumed that the current in the space of a bounded block flows through straight tubes without branching or passing from one tube to another. The tubes consist of a series of graphene stacks that follow one another at regular intervals.

Due to the orientational disorder of stacks in shungite, the possibilities of the tube model are rather limited. At the same time, it can be assumed that the statistical properties of the stacks are not very diverse in order to prevent the adequate use of the tube model. Next, we propose an algorithm that makes it possible to reduce the chaotic nature of the carbon structure to a regular model that allows the use of a tube model as a first approximation to the representation of an electrically conductive shungite model. To implement the model, direct images of the structure of shungite carbon were selected by scanning transmission electron microscopy (STEM).

2. Samples and measurement
For statistical analysis, samples were selected with a carbon content of ~98 % from the Maksovo deposit, which has an integral conductivity (2500 ± 200) S/m, and Nigozero deposit with a conductivity (1500 ± 150) S/m [4,11]. Structural data was obtained using STEM.

3. Results
3.1. Primary maps processing
Carbon distribution maps are a complex interweaving of black and white stripes corresponding to the ends of graphene layers and the gaps between them. A typical map obtained for the Maksovo sample is shown in figure 1a. Groups of parallel alternating dark and light stripes form stacks. In individual stacks, it is possible to distinguish the predominant directions of the alignment of the stripes, and also to determine the boundaries, beyond which the correct alternation of stripes is replaced by chaotically scattered dark and light areas. We have selected rectangular areas in which the stripes have a single direction (figure 1b). In what follows, we will call such regions “stacks”. Areas in which the stripes are not clearly marked will be referred to as “gaps between stacks”. For convenience, we replace the gaps with white boxes (figure 1c).

The orientation of the stacks layers is randomly, that is, over a large area of the field, all directions should be averaged. Therefore, at this stage of consideration, we will not attach importance to the orientation of the layers, but turn to the analysis of stacks by size (figure 1d). The areas of the stacks were calculated using the ImageJ program. The field size for the Maksovo sample is 16.90 × 13.30 nm, respectively, the field area is 224.77 nm². The total area of all stacks is 114.07 nm². For the Nigozero sample, in order to analyze a comparable number of stacks (35), we had to take a field size of 37.93 × 20.46 nm. The total area of all packs was 263.98 nm². The area distributions of the stacks (with a step of 0.5 nm²) are shown in figure 2. Taking into account the logarithmically normal form of the distribution, it will be optimal to calculate not the average, but the most frequent (modal) area of the stacks, which is (2.25 ± 1.26) nm² for Maxovo and (5.75 ± 2.64) nm² for Nigozero. If the stacks are represented as squares to simplify the model, then their sides will be (1.50 ± 1.12) nm and (2.39 ± 1.62) nm² for Maksovo and Nigozero, respectively.

3.2. Model of regular distribution of stacks
As an initial model approximation, we fill the field with square stacks spaced at equal distances between themselves (figure 3). Knowing the lengths of the sides of the squares of the stacks of our samples, we now find the dimensions of the gaps. Suppose that the gaps are the same, that is, the dimensions of the gaps along the Oₓ and Oᵧ axes are the same. Due to the periodicity of the structure in figure 3, it can be assumed that it is covered with identical single elements, each of which consists of one stack and the surrounding gaps below and on the right side (figure 3 – inset).
Figure 1. Map of carbon distribution in Maksovo shungite (a), map with selected stacks (b), identified stacks after removal of gaps (c) and after numbered (d).

Figure 2. Distribution of stacks on area (S) for Maksovo (a) and Nigozero (b).
Figure 3. Model representation of the structure of the map field. The shaded squares are stacks. The inset shows a diagram of a single element of the model map.

In this image, ABCD is a stack. The unit cell is the AEGI square. The area of this square is made up of the area of the stack ABCD and the total area of the gaps BEFC, DCHI and CFGH.

For the Maksovo sample, the total area of all gaps as the difference between the field area and the total area of all stacks is 110.70 nm². Area per space within one unit element is 3.35 nm². Denoting the length of the side of the stack through, and the width of the gap through, we can write the total area of the gap of a unit element in the form:

$$2ab + b^2 = S_{BE}.$$  \hspace{1cm} (1)

Solving this quadratic equation we get $b = 1.11$ nm. Thus, with a lognormal model of the size distribution of stacks, the side of the square of the Maxovo sample stack will be 1.50 nm, and the size of the gap between the stacks is 1.11 nm. For the Nigozero sample with a side of the square of the stacks of 2.39 nm, the gap size will be 2.11 nm.

3.3. Assessment of conductivity on the map

The relationship between the geometric dimensions of the stacks and the gaps makes it possible to estimate the integral conductivity of the sample as a whole. The ratio of the area occupied by the stacks to the area of the field gives the surface concentration of the stacks of 0.51. In [11] it is shown that to convert the surface concentration of a conducting region to a volumetric one, the value of the surface concentration should be raised to the degree of 3/2. Thus, for the Maksovo sample, we obtain the volume concentration of the stacks equal to: $0.51^{3/2} = 0.36$. For the Nigozero sample, the surface concentration of the stacks is 0.34; accordingly, the volumetric concentration will be 0.20. The conductivity is 2500 S/m for Maxovo and 1500 S/m for Nigozero [4,10]. The conductivity ratio is 1.66, and the ratio of the volume concentrations of stacks of graphene layers is 1.60. Thus, it can be assumed that the conductivity...
of noncrystalline carbon correlates with the concentration of stacks of graphene layers in the bulk of the sample and the size of the gaps between them. This makes it possible to assess the relationship between the structure and conductive properties of shungite, and in general, non-crystalline carbon.

It should be noted that the method of transmission electron microscopy does not allow visualization of all 100% of the stacks of graphene layers, since due to the anisotropy of the shungite structure, not all of them are turned by their end faces to the direction of the electron beam. In this case, such packs do not appear on the microscope image; in their place, as a rule, labyrinthine noise or blur is observed. However, given that with anisotropy we can observe a proportional number of stacks from their total number for each sample, we can assume that the revealed ratio of the stacks concentration corresponds to reality.

4. Conclusion
The role of graphene stacks in the formation of structural and electrical parameters of shungite carbon is considered. The study of the structure of shungite carbon by the STEM method was carried out, the result of which was a map of the spatial distribution of graphene layers and stacks consisting of these layers. Images of graphene stacks are highlighted on the map. Based on a statistical analysis of the areas of such regions, the most probable size of graphene stacks, as well as the gaps between the stacks, was found. A model of the regular structure of shungite carbon in the form of a periodic lattice of squares is proposed, the sides of which are equal to the average size of the stacks, and the intervals correspond to the average intervals between the stacks. Within the framework of the proposed model, the average concentration of graphene stacks in the total volume of shungite carbon was obtained. The dependence of the conductivity on the concentration of stacks of graphene layers in shungite is found.

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