Mapping of graphene layers by program identification based on Raman spectroscopy data

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Abstract This article discusses the basic methods of carbon structures research. Software has been proposed for determining the number of graphene layers based on the processing of spectral data obtained using Raman spectroscopy. The results of the analysis are presented in the form of micro-Raman maps of the distribution of the number of graphene layers.

1. Introduction
Carbon is one of the paramount substances necessary for life on our planet. Due to the ability of carbon atoms to connect in various ways, carbon-based systems exhibit various allotropic structures and properties. Certain allotropic states of carbon, such as diamond and graphite, have been known since ancient times, and some were discovered 10-20 years ago (fullerenes and nanotubes).

The first attempts to obtain a two-dimensional carbon structure were made long before the discovery of “real graphene”. For example, in 1962, the name graphene was born, when Hanns-Peter Boehm described the properties of carbon one atom thick [1]. In the works of Peierls and Landau (1935–1937), it was said that strictly two-dimensional (2D) carbon crystals are thermodynamically unstable and cannot exist [2-3]. This was one of the reasons why no one tried to obtain two-dimensional crystals before their discovery. Thermodynamic stability turned out to be possible due to thermal fluctuations that create a “ripple” – a waviness of the graphene surface with a height of ~5 nm.

The discovery of real graphene occurred in 2004, after publication in the journal Science [4], wherein it was reported about getting carbon monolayer was on an oxidized silicon substrate by dint of mechanical splitting. This technique consists in peeling off graphene flakes as a result of friction of crystalline graphite pieces against each other, or in “peeling off” them from the surface of graphite using a special adhesive tape with its subsequent dissolution. Micromechanical splitting of graphite became the main method of obtaining graphene in early studies of its properties, and also formed the foundation for a number of new methods of preparation, initiating active research in the field of graphite delamination. Graphene is a single-layer two-dimensional carbon structure organized into a regular hexagonal crystal lattice with carbon atoms at the vertices arranged in a plane. The properties possessed by graphene, make it a unique material, thus sought after by researchers. To date, developed many methods for obtaining graphene, due to the great interest in this material.

2. Graphene structure research methods
The main difficulty of graphene is its recognition and identification of the number of layers. In the initial studies, optical microscopy allowed significant progress in the identification of single-layer graphene.
The observations in [4–6] show that the use of optical microscopy is possible due to the placement of graphene on a silicon substrate coated with a thin layer of SiO$_2$. Conducting such a procedure leads to the appearance of an interference pattern, which is visible to an optical microscope. This interference pattern indicates the existence of graphene, but does not provide information on the number of layers.

The study of graphene using atomic force microscopy (AFM), is the most understandable way. This method consists in scanning the surface of the sample under investigation with a probe fixed at the end of the elastic console. The arising force acting on the probe causes the console to bend. By registering the level of bending, it is possible to control the force of interaction of the probe with the surface.

AFM provides information about the size of the structures on the nanometer scale, however, does not provide information on their chemical composition and crystallinity. Determination of the number of graphene layers, practically impossible, because of the chemical contrast between graphene and the substrate.

Raman spectroscopy is widely used in the study of carbon nanomaterials. Sensitivity to highly symmetric covalent bonds, such as carbon-carbon bonds, made it possible to track changes in the structure of the material. Information obtained by means of the Raman spectroscopy is determined by position of characteristic peaks, a form of peaks and their intensity [7]. The spectrum of carbon nanomaterials usually contains three main spectral lines: band G, band D, and band 2D (sometimes referred to as G'). G (1580 cm$^{-1}$) - a spectral line of the first order, very sensitive to deformation in the structure of the atom, can be used to study any changes in the geometry of the structure of graphene. D (1335 cm$^{-1}$), D' (2400 cm$^{-1}$) and D + D' - the spectral lines defining deformations and defects in crystal structure [8]. Graphene is usually characterized by one sharp and symmetrical peak of the 2D (2700 cm$^{-1}$) band. The high degree of orderliness and degree of crystallization in carbon nanomaterials is analyzed by the presence of a characteristic G-band and the absence of a D-band. The ratio ($I_D/I_G$) characterizes the degree of structural perfection of a graphene film. It is noteworthy that the intensities of the G line of single-layer graphene and bulk graphite are comparable, and the intensity of the D line of graphene and graphite is different. The D-line in graphene is a single sharp peak, and in graphite it is a strip consisting of two peaks $D_1$ and $D_2$, figure 1 (a).

![Figure 1](image)

**Figure 1.** Comparison of the spectra: a) comparison of the D-band at 514 nm at the edge of bulk graphite and single layer graphene (the fit of the D1 and D2 components of the D-band of bulk graphite is shown); b) the four components of the 2D-band in 2-layer graphene at 514 and 633 nm.

Graphite consists of several monolayers of graphene, the 2D-band observed in its spectrum is wider and asymmetric than the 2D-band in the spectrum of graphene, and shows the presence of several
components from several phonon modes: $2D_{1B}$, $2D_{1A}$, $2D_{2A}$, $2D_{2B}$; two of which, $2D_{1A}$ and $2D_{2A}$, have higher relative intensities than the other two, as shown in figure 1 (b).

The intensity ratio of the peaks ($I_{2D}/I_G$), allows to identify up to 5 graphene layers. For more than 5 layers, the Raman spectrum becomes difficult to distinguish from the spectrum of bulk graphite. Thus, Raman spectroscopy makes it possible to clearly distinguish one layer of graphene from two or more (up to 5) layers. The ratio of peaks ($I_{2D}/I_G > 2$) indicates graphene monolayer. In the case when the ratio ($I_{2D}/I_G < 1$), the number of layers can be estimated from the shape of the 2D peak.

Standard research methods do not provide a complete picture for understanding the properties of the material, since they change with increasing number of layers. Atomic force microscopy provides information on the size of structures of a nanometer scale, but does not provide information about their chemical composition or crystallinity. On the other hand, Raman spectroscopy allows to uniquely determine the chemical composition of the material. Combining these methods - chemically sensitive Raman spectroscopy and the "semi-contact" method of atomic force microscopy (AFM), makes it possible to obtain more complete information about the sample under study [9]. This technique allows to estimate the topology of the graphene structure: the number of graphene layers, the presence of chemical impurities, defects of the graphene structure [10].

3. Software identification of graphene layers

Based on the spectral peaks, it is possible to construct Raman distribution maps of G and 2D-peaks for the sample surface, characterizing the distribution of the number of graphene layers over the entire area of the formed structure. To solve this task, the specialized software, allows to identify and visualize the number of graphene layers on a solid substrate, was developed. The principle of operation is based on the processing of spectra, the fixation of changes in the positions and intensities of the spectral bands corresponding to graphene. For example, the G-band shifts with an increase in the number of layers from 1582 cm$^{-1}$ to 1579 cm$^{-1}$, due to the slightly higher frequency of the active Raman photon in graphene relative to graphite. Spectra can be used both to confirm the presence of the graphene phase and to determine the number of layers in graphene. The program analyzes the offset, width, and intensity of the D, G, and 2D-bands. The coefficients are calculated based on the ratio of peaks, which are compared with known values, satisfying a certain number of layers. The results of these changes are recorded in the software, and on the basis of the coefficients, micro-Raman maps are constructed, which are a set of tiles of different colors. The colors of the tiles on the map correspond to a certain number of layers, which makes visualization of the result more convenient for perception.

Figure 2 shows the graphical user interface of the software displays the results of intensity ratios $I_{2D}/I_G$ evaluation for graphene samples.

![Figure 2. Visualization of the intensity ratios $I_{2D}/I_G$ evaluation in comparison with original image generated by Raman spectrometer.](image)
Samples of graphene were obtained by laser synthesis of graphene structures [11-13]. The main idea of the method is to process a graphite sample immersed in a liquid nitrogen medium with femtosecond laser radiation. The physical meaning lies in the heat-conducting property of graphite, as well as the change in its structure at low temperatures. The thermal expansion of the graphite lattice is anisotropic; it manifests itself more strongly if the lattice order is higher. In the direction perpendicular to the basic planes, the coefficient of thermal expansion is positive, practically independent of temperature, and more than 20 times higher than the average absolute value for the basal planes. Consequently, the temperature coefficient of linear expansion in the direction of the basal planes is much less than in the perpendicular direction, thereby contributing to the separation of the structure with intensive heating.

4. Conclusion
Thus, the main methods of carbon structures research, such as optical microscopy, atomic force microscopy and Raman spectroscopy, were considered. For identifying the number of graphene layers was developed the software, provides a qualitative analysis of graphene structure perfection degree and allows to weed out the spectra belonging to substrates of deposited graphene structures. Thanks to software automation it became possible to create Raman maps with different colors corresponding to a certain number of layers.

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