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DEVELOPMENT OF IMPROVED TECHNOLOGY FOR PRODUCING GRAPHENE-LIKE COATING BY LPCVD METHOD

The object of research in this work was the coating of oxygraphene on a silicon single crystal substrate. In the work, the LPCVD (Low Pressure Chemical Vapor Deposition) method of deposition from the gas phase at low pressure is used to obtain graphene-like coatings on heat-resistant materials. A feature of the proposed LPCVD method in comparison with the classical method of deposition from the gas phase CVD (Chemical Vapor Deposition) by the method of catalytic decomposition of carbon-containing gas followed by the deposition of a graphene-like coating on a copper template is the use of a higher partial gas pressure, which leads to the deposition of graphene-like waste not only on the surface of the copper template-catalyst, but also in the entire volume of the reaction chamber and the materials introduced into it. A monocrystalline silicon template was used as a model for coating. The resulting coatings of different thicknesses were examined by scanning electron microscopy, Raman spectroscopy, and density was assessed by helium pycnometry. Based on the analysis of the results obtained using the method of scanning electron microscopy, the possibility of varying the thickness of the oxygraphene coating was shown. In addition, the formation of oxygraphene on a silicon single crystal substrate was confirmed by the Raman spectroscopy method, namely the presence of characteristic peaks in the spectra of the studied materials. Using the helium pycnometry method, a decrease in the density of the coated material from 2.25 g/cm^3 to 2.08 g/cm^3 was found. It was established that the greater the coating thickness, the lower the density. The general analysis showed that the developed LPCVD technology allows obtaining an oxygraphene coating on materials of any shape, porosity, size and resistant to temperatures above 600 °C in order to functionalize their surface and improve and improve their properties.

Keywords: *graphene, oxygraphene, coating, LPCVD method, CVD method, microstructure, Raman spectroscopy, density.*

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1. Introduction

Graphene and graphene-like materials are a broad class of modern nanostructured two-dimensional materials with a potentially wide range of applications. Due to high chemical and corrosion resistance, specific electrical and thermal conductivity, graphene and graphene-like materials (GLM) are already widely used in many areas of production. The most common areas of application of GLM are the creation of various anti-corrosion, tribological and anti-friction and other coatings based on them, the main purpose of which is to make the surface of the carrier material work to provide new, uncharacteristic properties. The demand for such materials determines the constant development of their production methods, and the uniqueness of their properties is due to the involvement of an increasing variety of methods for their characterization [1–5].

Graphene-like materials include: monolayered graphene (MLG), bilayered and multilayered graphene (BLG and MLG), carbon nanotubes (CNT), graphene oxide (GO), reduced graphene oxide (rGO), etc. [6, 7].

The main methods of obtaining such materials are mechanical exfoliation, Chemical Vapor Deposition (CVD), Electrophoretic Deposition (EPD), Solid Phase Synthesis (SPS), Laser-Assisted Synthesis (LAS), epitaxial growth, pyrolysis production, organic synthesis, etc. [5, 7].

Today, the vast majority of established methods for obtaining graphene and graphene-like materials are variants of the CVD method, which make it possible to obtain structurally controlled materials and coatings. However, the search for more technological, cheap and accessible production methods is still ongoing, including those that would allow not only to produce GLM in industrial quantities, but also to create simple and affordable technologies for their production.

In this paper, LPCVD (Low Pressure Chemical Vapor Deposition) is proposed – a method similar to CVD in the process of synthesizing graphene-like materials with the simultaneous use as a catalyst and, at the same time, as a substrate for the deposition of a GLM layer, copper foil. LPCVD differs from the traditional CVD method in that the pressure and, accordingly, the concentration of carbon-containing gas in the working chamber of a tubular quartz vacuum furnace is achieved much higher than during the deposition of mono-bi- or multilayer graphene. At the same time, the deposition process begins not only on the surface of the copper substrate, but also in the entire volume of the chamber and the materials introduced into the chamber. In this case, the deposition of a graphene-like coating is observed, including, on the inner surface of the pores of porous materials and powders with a developed specific surface, which is an advantage of the proposed method. In this way, it is possible to cover any heat-resistant (over 600 °C) materials, such as glass, most metals, ceramics, etc., with a graphene-like coating. The thickness of the coating can be adjusted within wide limits, the concentration (pressure) and type of supplied carbon-containing gas, the temperature of the process and the number of heating-deposition cycles.

Thus, *the aim of research* is to develop an improved technology for obtaining a graphene-like coating by the LPCVD method, to study its structure and properties in order to further functionalize the surface of materials for various purposes.

2. Materials and Methods

The object of research is the coating of oxygraphene on a silicon single crystal substrate. An uncoated single crystal silicon substrate served as a control for comparison.

The microstructure of the resulting coating was studied by scanning electron microscopy using a Tescan Mira 3 LMU microscope (Tescan, Czech Republic).

Micro Raman measurements were performed at room temperature in backscattering geometry using a Horiba Jobin Yvon T-64000 Raman spectrometer (Horiba, Japan) equipped with an Olympus BX41 microscope. The Ar-Kr ion laser line with a wavelength of 488 nm was used for excitation. The laser beam was directed onto the surface of the sample using a 50x/NA 0.75 objective, forming a spot with a diameter of approximately 1 μm. The laser power on the sample surface was limited to less than 1 mW to prevent structural damage or heating.

The density of the initial silicon single crystal and with a graphene-like coating of different thicknesses was measured using a helium pycnometer (AccuPyc II 1340, Micromeritics, USA) at 24±2 °C, according to ISO 12154:2014. Before measurements, the materials were dried at 150 °C for 2 hours in a vacuum (VacPrep 061 Sample Degas System, Micromeritics, USA).

3. Results and Discussion

The coating was applied by the LPCVD method using the following operations:

1. Loading single crystal silicon substrates and catalyst (1 dm^2 of thin copper tape twisted in a spiral was used in the experiment) into a tubular quartz vacuum furnace.
2. Sealing of the working zone of the furnace and pumping to a residual pressure of ≤0.1 kPa.
3. Washing of the working area by means of a smooth (at a speed of 1 kPa/s) injection of inert gas (dried nitrogen) up to a pressure of 100 kPa.
4. Pumping the working zone to a residual pressure of ≤0.1 kPa with simultaneous heating of the working zone to 600 °C and holding for 30 minutes.
5. Inflow of carbon-containing gas (propane/butane) to a residual pressure of 50 kPa at a rate of 1 kPa/s.
6. Cooling to a temperature in the working chamber ≤50 °C.
7. Air intake, depressurization of the working area of the furnace and extraction of experimental samples.

To obtain a multilayer coating with a greater thickness of the oxygraphene layer, the procedure described in paragraphs 3–4 are repeated several times (the more cycles, the thicker the coating). Single and 5-fold application was used in the work. The scheme of the process is shown in Fig. 1.

Fig. 2 shows the microstructure of an oxygraphene layer on a single-crystal silicon substrate, which indicates a continuous coating of uniform thickness with a characteristic broken relief surface typical of graphene-like layers.

Fig. 3 shows the spectra of Raman scattering of light obtained from a silicon substrate covered with graphene-like structures. The spectra are dominated by two prominent peaks, namely peak D (~1345 cm^{-1}) and peak G (~1600 cm^{-1}), as well as less intense and broadened two-phonon combinations 2D, D+G and 2G (~2900 cm^{-1}), which are typical features of disordered or partially oxidized graphene [9, 10]. In addition, single-phonon LO-TO (~521 cm^{-1}) and two-phonon 2LO (~950–980 cm^{-1}) bands of single-crystal Si are recorded for a single coating.

Fig. 4 shows the results of determining the skeleton (pycnometric) density for a silicon substrate without and with an oxygraphene coating of different thickness, obtained by single and multiple coating. The samples showed a slight decrease in density in the presence of a coating, and the thicker the coating, the lower the density.

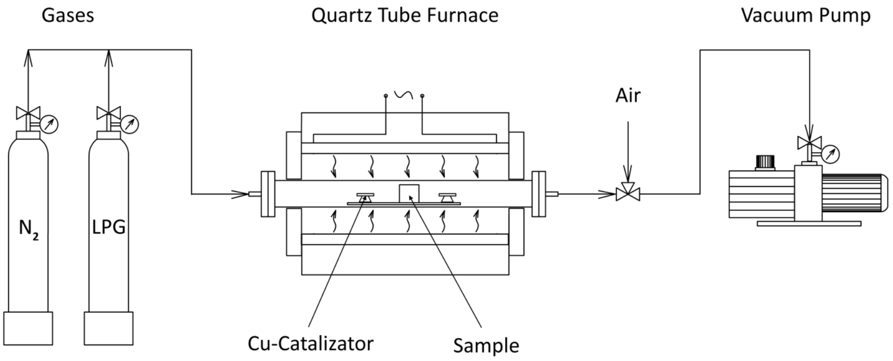
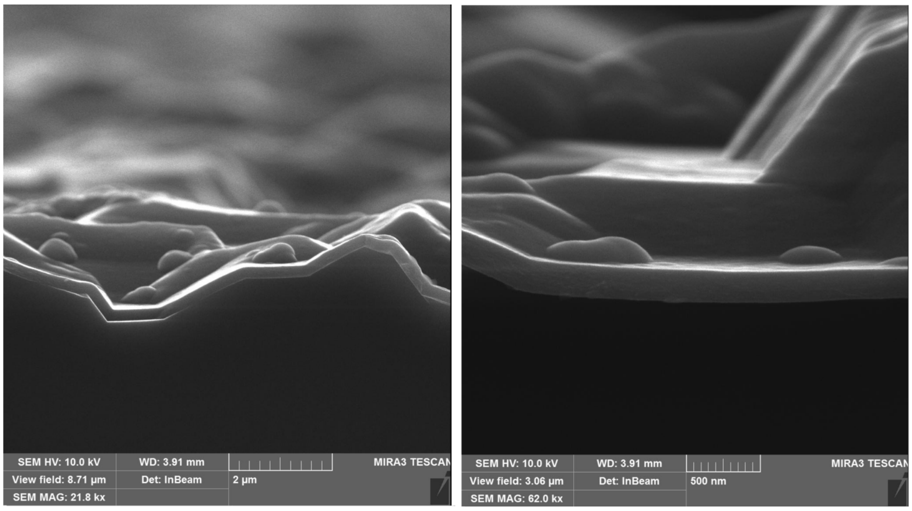


Fig. 1. Scheme of obtaining a graphene-like coating by the LPCVD method [8]



a *b*

Fig. 2. Microstructure at different magnifications (*a* – ×21800 and *b* – ×62000) of the oxygraphene coating on a single crystal silicon substrate

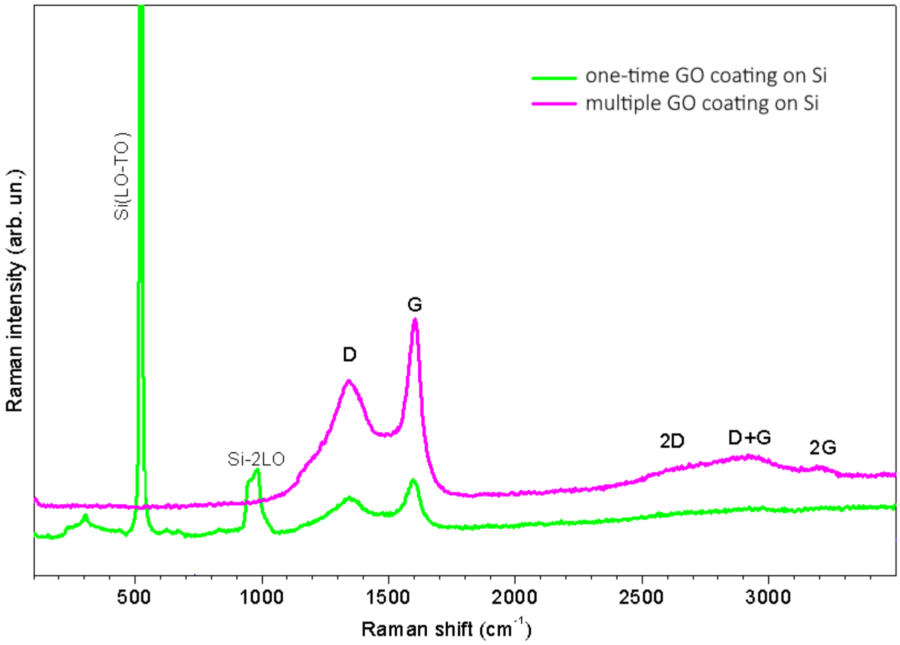


Fig. 3. Raman spectra of oxygraphene coating of different thicknesses on a silicon single crystal substrate

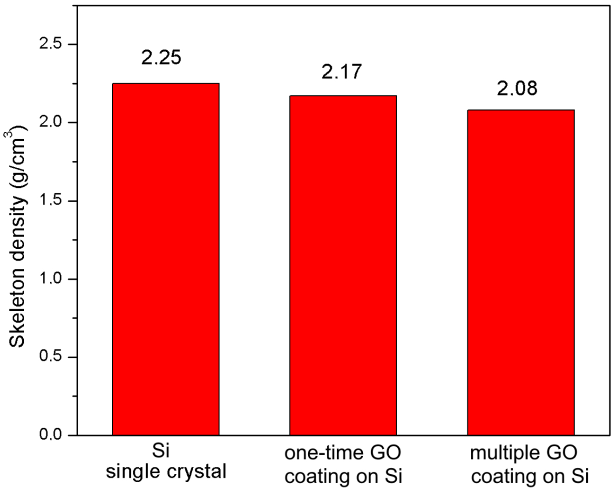


Fig. 4. Results of determining the skeleton (pycnometric) density

Practical meaning. As already mentioned above, the use of graphene-like coatings is finding new fields of application, and the development of new approaches and methods of their production is a promising area of materials science development. From a practical point of view, the proposed improved LPCVD method for obtaining GLM is a simple and technological way to create a uniform dense coating with adjustable thickness, and can be used for the production of functional coatings based on GLM in any field of science and technology where similar materials can be used. namely, to create: anti-corrosion, heat-resistant, electrically conductive, semi-conductive, anti-friction, mirror, bioactive and other types of coatings.

Research limitations and prospects for its further development. The limitation on the application of the proposed method is only the heat resistance of the substrate material – the basis on which the GLM should be applied. The proposed method makes it possible to successfully apply a graphene-like coating on materials resistant to high temperatures (600 °C and above), such as ceramics, most metals and their alloys, cermets, sieves, heat-resistant glass, including quartz, and widely used semiconductor materials – silicon and germanium. The author is currently conducting research, the purpose of which is to reduce the lower temperature limit of the application of the method to 500 °C, which will make it possible to obtain a high-quality continuous graphene-like coating to increase the heat-resistant properties of structural alloys based on aluminum, as well as on silicate glass, the temperature of the beginning of deformation of which is within 540–560 °C.

The influence of martial law conditions. The state of war in Ukraine did not affect the conduct of research and/or the obtained results, since the majority of them were obtained before the start of its implementation. Recently, the results were checked and summarized. The author hopes that the obtained results will be able to increase the defense capability of the state, if they find their application in the defense field.

4. Conclusions

An improved LPCVD method for obtaining graphene-like coatings has been developed. A silicon single crystal was used as a model.

The results of SEM confirmed the obtaining of a continuous coating of uniform thickness with a characteristic refracted relief surface typical of graphene-like layers.

The formation of oxygraphene on a silicon single crystal substrate was confirmed by Raman spectroscopy.

Density control by helium pycnometry showed a decrease in the density of single crystal silicon with a graphene-like coating from 2.25 g/cm^3 for pure silicon to 2.08 g/cm^3 for silicon with a multilayer graphene-like coating.

It is shown that the developed technology makes it possible to obtain graphene-like coatings on materials stable at temperatures above 600 °C of any shape, porosity and size, with the aim of improving their properties due to surface functionalization.

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Conflict of interest

The author declares that he has no conflict of interest in relation to this study, including financial, personal, authorship, or any other, that could affect the study and its results presented in this article.

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Data availability

The manuscript has no associated data.

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