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The Raman Diagnostics of Carbon Films Obtained by Electron-beam Deposition on Cu, Al and Ni Substrates

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Results of studies by Raman spectroscopy of the structural features of carbon films obtained by electron-beam physical vapor deposition (EB-PVD) of graphite vapor flow depending on the substrate material (Cu, Al, Ni) and the deposition time are described in this paper. Different carbon microstructures are effectively formed in a wide range of conditions, therefore, various methods and approaches are used in their synthesis. A feature of the method used by the authors for obtaining carbon films is a significant (by an order) intensification of the evaporation process of graphite by using an intermediate bath of molten tungsten. Molten tungsten has higher temperature and lower vapor elasticity compared to carbon and provides an intense and uniform carbon vapor flow. Above the crucible from which carbon evaporates, tungsten plates are placed, which serve as a reflector of the vapor flow oriented in a plane at an angle of 45°, that ensure maximum reflection of evaporated carbon on foil substrates made of different materials (Ni, Cu and Al). The substrate material has a significant influence on the phase composition and structure of the deposited carbon films. The Raman spectra of carbon films deposited on aluminum and copper substrates are similar, and the structural parameters of the resulting carbon films do not differ significantly depending on the substrate material. Among the analyzed carbon films, the most advanced with the least number of structural defects are the films obtained by deposition of the vapor flow on nickel substrates. The results of the study confirm the possibility of graphene obtaining by EB-PVD of graphite evaporation through an intermediate bath of molten tungsten and subsequent condensation of the reflected flow on substrates made of the selected materials.

Keywords: Carbon, Electron-beam deposition, Raman spectroscopy, Structure.

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1. INTRODUCTION

In recent years, significant progress has been made in the study and practical application of nanostructures, in particular graphene, which provides a basis for a deep understanding of the properties of the full range of nanostructured carbon materials and composites with their content. Today, graphene is one of the most promising materials in modern nanoelectronics [1]. The prospects of its use for solar cells, supercapacitors, optoelectronic devices, bio-sensors, SERS substrates and nanofluids have already been demonstrated. Its fundamental properties are radically different from 3D materials [2]. The properties of graphene may differ depending on the method of its production, because it changes the size of graphene flakes, the number of vacancies, marginal and other defects. Beside this, the properties of graphene are significantly affected by the characteristics of the substrate [3] on which it was deposited.

Nowadays, in most cases, graphene is obtained by methods of intercalation of graphite, CVD-epitaxial, graphitization of SiC at high temperature, and others. These methods currently do not guarantee to obtain a material with a predetermined number of defects and sizes, which is necessary for the use of graphene in the manufacture of nano- and optoelectronic devices. Therefore, the search, development and implementation of effective methods for obtaining graphene and thin films based on it is currently an urgent scientific and technological task.

Widespread practical application of electron-beam physical vapor deposition (EB-PVD) is primarily due to the relatively high productivity of the processes and opens up prospects for obtaining carbon materials with different micro- (nano-) crystalline structure [4].

Raman spectroscopy has proven to be an effective method for diagnosing carbon structures (graphite, fullerenes, carbon nanotubes, carbine, diamond, graphene) [3]. For each of these materials, there are characteristic bands in the Raman spectrum, and the shape, frequency and intensity of such bands allow them to be quantified (Fig. 1) [6].

The use of Raman spectroscopy for the diagnosis of carbon structures during their cultivation allows to

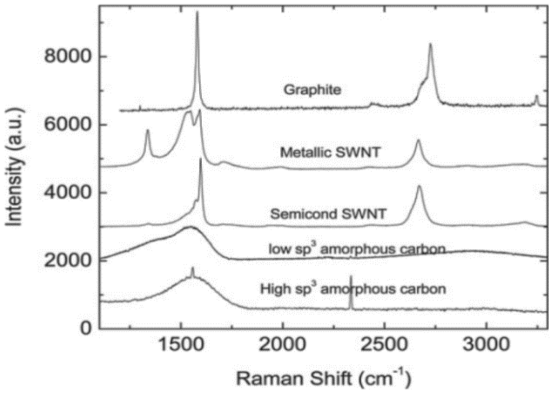

Fig. 1 – Raman spectra of different carbon structures [6]

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control the formation of a modification or their mixtures and to analyze the influence of technological parameters on their properties.

2. EXPERIMENTAL

The aim of this work is to determine the effect of the substrate material on the properties of carbon films obtained by EB-PVD method. The paper presents the results of research by Raman spectroscopy of carbon films obtained by electron beam deposition of carbon on Cu, Al and Ni substrates.

Since EB-epitaxy was used to grow graphene and carbon films, a feature of our deposition method was evaporation of graphite through a molten tungsten bath. The presence of a tungsten melt with a lower vapor pressure than carbon has provided an intense and uniform vapor flow of carbon.

Carbon films for this research were formed by the method of electron beam evaporation of carbon through molten tungsten in vacuum and followed by condensation of the reflected vapor flow using a tungsten screen [4]. For this purpose, MG-1 commercial graphite was evaporated by an electron beam with a power of 24.2 kW, vacuum in the technological chamber during deposition was (6-9)·10^{-2} Pa. Cu, Al and Ni foils with a size of 250 × 25 × 0.1 mm were used as substrates. Technological time (duration) of formation of carbon films was, respectively, 180 s (G1), 18 s (G2) and 2 s (G3).

The formed carbon films were examined by Raman spectroscopy in a laboratory facility, which is a double monochromator "DFS-52" equipped with a CCD camera "Andor" for recording spectra and a microscope. To obtain the spectrum, the radiation of a solid-state laser with diode pumping (DPSS) of the visible (blue) spectral range of coherent radiation (with a length of 457 nm) was used. The geometry of the experiment was constructed in such a way that the exciting and scattered laser radiation focused on the carbon films was collected by a single lens.

3. RESULTS AND DISCUSSION

Fig. 3 shows the Raman spectra of carbon films deposited at different modes (G1, G2, G3) on Al, Cu and Ni substrates, respectively, depending on the time of their deposition.

To determine the parameters of individual bands, the obtained experimental Raman spectra were decomposed into Gaussian components I_D/I_G, and the average sizes of nanocrystals in the carbon films were estimated. The obtained values are given in Table 1.

Table 1 – Structure parameters of the obtained carbon films

samples	ω_D, cm^{-1}	Γ_D, cm^{-1}	ω_G, cm^{-1}	Γ_G, cm^{-1}	I_D/I_G	I_{2D}/I_G	L, nm
G1_Cu	1356	127	1595	67	1.85	0.43	5.6
G1_Ni	1352	46	1583	61	1.12	0.98	9.3
G1_Al	1365	192	1590	90	1.53	0.43	6.8
G2_Cu	1367	203	1588	109	1.36	0.66	7.6
G2_Ni	1355	47	1589	71	0.59	1.13	17.6
G2_Al	1368	241	1578	125	1.32	0.68	7.9
G3_Ni	1376	175	1583	105	1.19	0.61	8.7
G3_Al	1348	132	1581	110	0.59	0.74	17.6

The number of defects in carbon films can be estimated by the half-width (G) of the bands D and G, as well as by the ratio of intensities I_D/I_G.

Comparison of the obtained average sizes of nanocrystals (Table 1) indicates an increase in the ratio of intensities I_D/I_G with decreasing carbon crystal size, regardless of the substrate material and deposition time (see Fig. 2), which agrees satisfactorily with the data of [7].

The structural parameters of the carbon films depending on the substrate material and deposition time are given in Table 2.

Table 2 – Structural parameters of the carbon films obtained on Al and Ni substrates during different time of deposition

Deposition time, s	Al substrate			Ni substrate		
	Γ_D, cm^{-1}	Γ_G, cm^{-1}	I_D/I_G	Γ_D, cm^{-1}	Γ_G, cm^{-1}	I_D/I_G
2	132	110	0.59	175	105	1.19
18	241	125	1.32	47	71	0.59
180	192	90	1.53	46	61	1.12

Comparison of the obtained data (Table 2) shows that the ratio of intensities I_D/I_G decreases with decreasing thermal conductivity of the substrate material and increases with increasing deposition time. The ratios of intensities I_D/I_G for the carbon films deposited at 18 s on Cu and Al substrates are almost at the same level (1.36 and 1.32, respectively).

Analysis of the results (Table 2) allows us to draw the following conclusions:

- the most perfect carbon films (with the least number of defects) are formed on Ni substrate formed within 18 and 180 s;
- the half-width (G) of the D and G bands for these films is the smallest and is 47 and 71 cm^{-1} and 46 and 61 cm^{-1}, respectively;
- the ratio of intensities I_D/I_G for these films is minimal and is 0.59 and 1.12.

Given the lower thermal conductivity of Ni compared to Cu and Al and other similar technological parameters, the deposition of carbon films on Ni substrate occurred at elevated temperatures, which had a positive effect on the perfection of the structure of the obtained carbon films [9].

It is known that for graphene, as well as for graphite, the so-called G band (~ 1582 cm^{-1}) is always manifested in the first-order spectrum [8]. In the presence of defects in the carbon structures, the so-called D (~ 1350 cm^{-1}) and De' (~ 1620 cm^{-1}) bands appear in the spectrum.

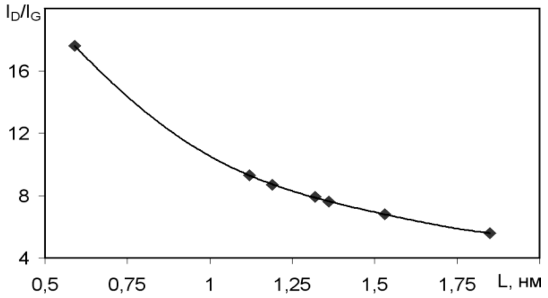


Fig. 2 – Dependence of intensity ratio I_D/I_G on size of carbon crystallites L, nm

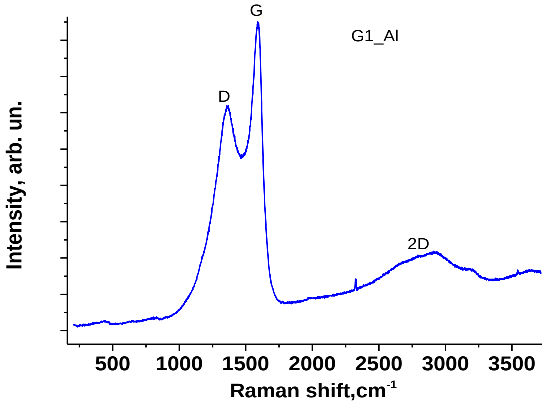
The G-band is associated with the doubly degenerate symmetry mode E2g of the center of the Brillouin zone and is the result of tensile oscillations of all pairs of carbon atoms that have *sp*² hybridization and are part of benzene rings [5]. The D-band is a manifestation of A1g modes (at K-point at the Brillouin zone boundary) of *sp*²-hybridized carbon atoms in benzene rings and is recorded in the Raman spectrum only for samples with structural defects, because in defect-free carbon structures it is prohibited by sampling rules [6].

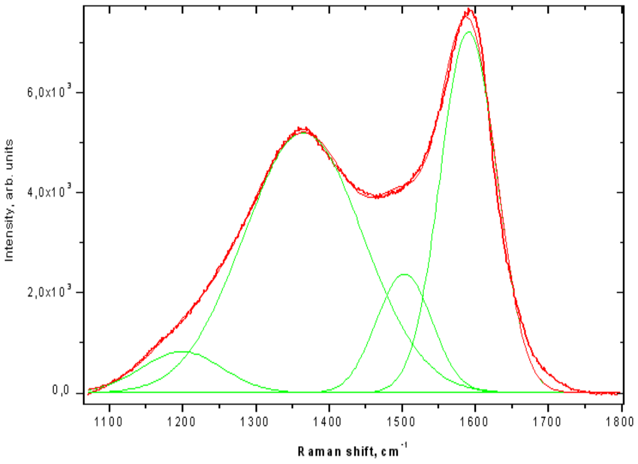
Analysis of the obtained experimental Raman spectra of carbon films (Fig. 3) deposited on Al and Cu substrates shows that the D and G bands appear in the first-order spectrum and the 2D band – in the second-order spectrum. In this case, their Raman spectra are similar; in particular, the frequency positions of all bands coincide. The intensity of the 2D band is less than the intensity of the G band, and with increasing deposition time, the ratio of intensities I_{2D}/I_G decreases and is almost independent of the substrate material.

In the Raman spectrum of carbon films deposited on Ni substrate, D and G bands appear in the first-order lines and 2D, D + D' and 2D' bands – in the second-order spectrum; and both Raman spectra are quite similar. In particular, the frequency positions of all bands coincide, and the intensity of the D band in the samples deposited at 180 s is slightly higher. This indicates that with increasing deposition time (higher temperature), more defects are formed in the film. The presence of two components in the second-order 2D band in carbon structures indicates the existing vertical ordering between the individual graphene layers in these structures [8].

From the obtained Raman spectra of carbon films it is seen that the parameters of the characteristic D, G, and 2D bands change significantly depending on the substrate material and technological conditions of deposition. In particular, in addition to temperature, the deposition time also has a significant effect on the structure of condensates. The most perfect carbon films are formed by deposition on Ni substrate for 18 and 180 s and correlate satisfactorily with paper [9].

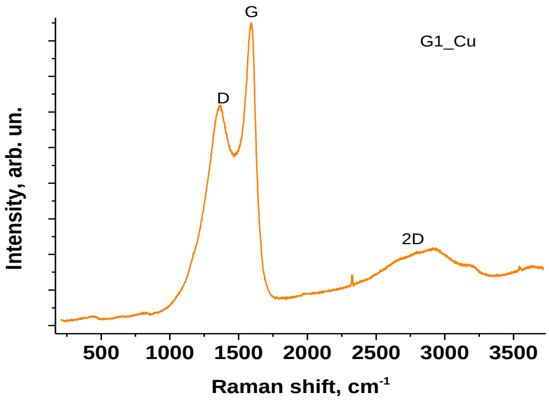
a) Al-substrate

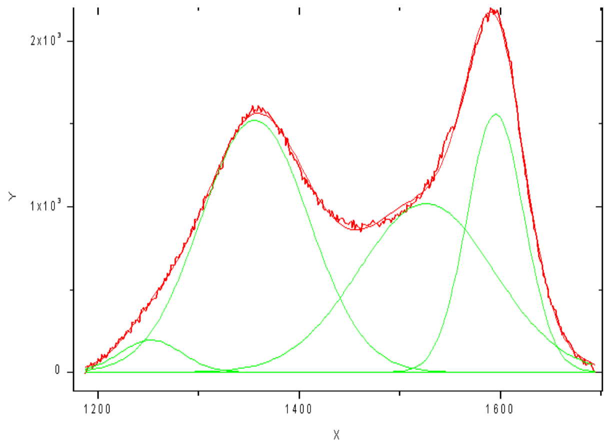




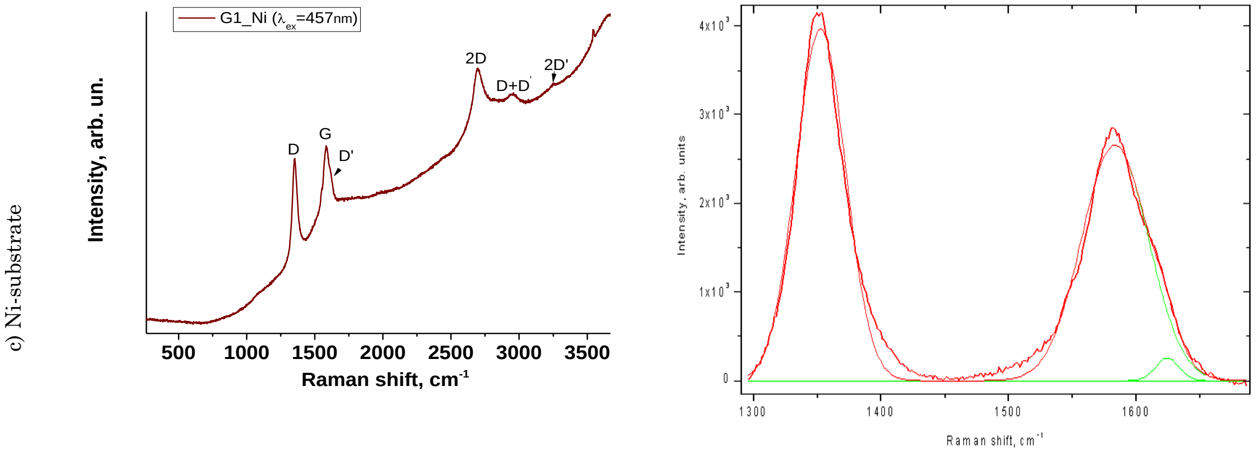
spectrum decomposition in the range of D and G bands into components

b) Cu-substrate





spectrum decomposition in the range of D and G bands into components



spectrum decomposition in the range of D and G bands into components

Fig. 3 – Raman spectra of the carbon films deposited on Al (a), Cu (b) and Ni (c) substrates during 180 s

The evaluation of the sizes of the obtained graphite nanocrystals indicates that the largest graphite nanocrystallites were formed in the most perfect films, which are G1_Ni and G2_Ni. The characteristics of carbon films obtained from Raman studies indicate possible ways to further improve the technological process of graphene film formation: determination of optimal deposition temperature, electron beam power, deposition time of carbon films and substrate material, and parameters of heat treatment (annealing) of carbon films (temperature, time).

As noted above, graphene is characterized by the ratio of band intensities $I_{2D}/I_G > 1$. The results obtained (Table 1) showed only in one case the ratio $I_{2D}/I_G > 1$ – for the G2_Ni film. Thus, it can be summarized that the most perfect of the studied samples is a carbon film obtained by EB-PVD of graphite on Ni substrate for 18 s.

4. CONCLUSIONS

The substrate material has a significant effect on the phase composition and structure of deposited carbon films.

Among the analyzed samples, the most perfect structures with the least quantity of defects are the films obtained by vapor deposition on Ni substrates for 18 s. These carbon films are characterized by the smallest half-width (G) of the D and G bands of 47 and 71 cm^{-1}, respectively, as well as the maximum intensity ratio I_{2D}/I_G of 1.13.

The results of the research indicate the possibility of obtaining graphene by the technology of electron-beam evaporation of graphite through molted tungsten and its condensation of reflected vapor flow on a substrate made of the selected material.

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Раманівська діагностика вуглецевих плівок, отриманих електронно-променевим осадженням на підкладках з Cu, Al та Ni

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У роботі наведено результати досліджень методом раманівської спектроскопії особливостей структури вуглецевих плівок, отриманих електронно-променевим осадженням парового потоку графіту в залежності від матеріалу підкладки (Ni, Cu, Al) та часу осадження. Різноманітні вуглецеві структури ефективно утворюються в широкому діапазоні технологічних параметрів їх отримання, тому при їх синтезі використовується багато різних методів та підходів. Особливістю використаного методу осадження була суттєва (на порядок) інтенсифікація випаровування графіту шляхом використання ванни-посередника з розплавленого вольфраму. Наявність розплаву вольфраму з високою температурою та більш низькою, ніж у вуглецю, пружністю пари забезпечує одержання інтенсивного і рівномірного парового потоку вуглецю. Над тиглем, з якого випаровується вуглець, розташовували вольфрамові пластини – відбивача парового потоку (рефлектор), який орієнтували в площині під кутом 45°, що забезпечувало максимальне відбиття випаруваного вуглецю на підкладки із фольги, виготовленої з різних матеріалів (Ni, Cu та Al). Матеріал підкладки має суттєвий вплив на фазовий склад та структуру осаджуваних вуглецевих плівок. Раманівські спектри вуглецевих плівок, осаджених на алюмінієвій і мідній підкладках, є подібними. При цьому структурні параметри одержаних вуглецевих плівок суттєво не відрізняються в залежності від матеріалу підкладки. Серед проаналізованих вуглецевих плівок найбільш досконалими з найменшою кількістю структурних дефектів є плівки, отримані осадженням парового потоку на підкладках з нікелю. Результати проведених досліджень підтвердили можливість отримання графену способом EB-PVD з випаровуванням графіту через ванну-посередник з наступною конденсацією відбитого парового потоку вуглецю на підкладках з обраного матеріалу.

Ключові слова: Вуглець, Електронно-променеве осадження, Раманівська спектроскопія, Структура.