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Formation of vertical graphene on surface of the gallium-arsenide structures

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The properties of carbon layers (C-layers) formed by thermal decomposition of CCl_4 at temperatures of 600−700°C on the surface of gallium arsenide structures fabricated by MOC-hydride epitaxy on n^+-GaAs (100) wafers have been studied. The surface morphology of the carbon layers was studied using atomic force microscopy. The structural and optical properties were studied using Raman spectroscopy and reflection spectroscopy. It has been found that in the case of a C-layer fabricated at a temperature of 650−700°C, the atomic force microscopy image demonstrates the presence of vertical carbon nanowalls (vertical graphene) located parallel to one of the [110] directions of the GaAs crystal lattice. The characteristics of the bands observed in the Raman spectra correspond to the parameters of the spectra of vertical graphene. The reflectivity coefficient of such carbon layers significantly decreases (diffuse reflection does not exceed 25% for a layer fabricated at 700°C) in the wavelength range from 0.19 to 1.8 μm. The presence of a significant „absorbing" ability makes the obtained carbon layers promising as a conducting contact in photosensitive semiconductor device structures, which is confirmed by preliminary results of studies of the current-voltage characteristics and spectral dependences of the photocurrent.

Keywords: thermal decomposition of carbon tetrachloride, gallium arsenide, vertical graphene morphology.

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1. Introduction

Recently, among the studies focused on different graphene-based structures inheriting remarkable parameters of this material (in particular, mechanical strength and flexibility, developed specific surface area) a number of works appeared devoted to the production, investigation of properties and application of vertical graphene (VG) [1]. In essence, the vertical graphene is understood to be an array of vertically-aligned spatially separated carbon nanosheets of different shape that have thicknesses of several graphene layers with a typical interlayer distance of about 0.34 nm [2]. As compared to common graphene films (including multilayer graphene) vertical graphene features a developed morphology, sharp edges, a large surface-to-volume ratio. These features of vertical graphene define the prospects of its use as field emitters, gas sensors and biosensors, solar cells, etc. [3,4].

According to publications (see reviews [1,5]) plasma-enhanced chemical vapor deposition (PECVD) is considered virtually the only method to produce structures of vertical graphene. At the same time, plasma can be produced by different ways [5], for example, with the use of microwave (usually about 2.45 GHz) of HF source (13.56 MHz). Dependencies of parameters of VG structures grown by this method on the modes of their production have been studied [6]. However, the effect of plasma on the surface of substrates in the process of deposition may have negative consequences for semiconductor structures. Therefore, the search for alternative methods to form VG first of all on the surface of such materials as, for example, GaAs, is of scientific and practical interest.

In this study a carbon graphene-like layer containing vertical nanowalls (vertical graphene) is formed on the surface of gallium-arsenide quantum-confined structure by the method of thermal decomposition of carbon tetrachloride in hydrogen flow. For the purpose of use in devices, morphology, structure, optical and electrical properties of the produced samples have been studied.

2. Experiment procedure

Structures with carbon layer on the surface were produced on n^+-GaAs(100) substrate in a metal-organic chemical vapor deposition (MOCVD) reactor at the atmospheric pressure. The following samples were successively grown at a temperature of $T_g = 600{-}650^\circ$C: a buffer layer of n-GaAs (Si-doped to a concentration not more than 10^{17} cm^{-3}) with a thickness of $\sim 0.5\,\mu$m, a quantum well of InGaAs (with a thickness of 8−10 nm with In content of $x \sim 0.12$) and an undoped cap layer of GaAs with a thickness of 20 or 50 nm. Then the method of thermal decomposition of CCl_4 was used to form a carbon film [7]. This method allows forming carbon films in the same reactor where the epitaxial growing of semiconductor layers is implemented, therefore the formation of C-layer can be embedded into the process of producing the device semiconductor structure. When forming a carbon film, temperature of the process (T_{gC}) varied from 600 to 700°C and the content of CCl_4 in the hydrogen flow varied as well. Table 1 presents a brief process description of the produced gallium-arsenide structures with a carbon layer on their surface. The Raman scattering (RS) studies of carbon films were carried out by a NTEGRA SPECTRA (NT-MDT) setup at room temperature in the backscattering geometry with the use of a laser with a wavelength of 473 nm. The radiation was focused by a 100× lens with an aperture of NA = 0.95 to a spot with a diameter of $\sim 1\,\mu$m. The power of unfocused laser radiation measured by a 11PD100-Si silicon photodetector (StandaLtd) was varied in the range from 1 mW to $1\,\mu$W. The RS spectroscopy was carried out in the range of $500-3500\,cm^{-1}$ with a resolution of $3\,cm^{-1}$.

Morphology of surface of the carbon layers was investigated by atomic-force microscopy (AFM). The AFM studies were carried out using a SmartSPM atomic-force microscope (AIST-NT, currently it is manufactured by HARIBA Scientific). AFM-images were taken in the vertical mode [8,9] developed by authors of the study. This technique features a number of benefits compared with the commonly used mode of scanning that assumes a feedback to keep fixed distance from the probe tip to the sample surface. Vertical mode allows taking images without distortions even in the case of large height differences and the presence of vertical walls. This mode is the most safe technique in terms of integrity of the probe and the sample. Vertical mode gives the possibility to use very sharp probes for scanning of fragile and easy-deformable surfaces. In this study the scanning was carried out by cantilevers where thin „whiskers“ were preliminary built-up following the procedure described in [10].

Optical properties of the produced structures with wavelength varying from 0.18 to $1.8\,\mu$m were studied by the method of reflectance spectroscopy at nearly normal incidence using a Cary 6000i spectrophotometer (Varian). Diffuse reflectance spectra were taken with the use of DRA-2500 external accessory by a Cary 5000 double-beam spectrophotometer (Varian) in the wavelength range from 0.19 to $0.8\,\mu$m.

To study electrical properties of structures, 2×2 mm samples were cut out. Chemically and mechanically resistant carbon film played the role of the top conductive contact. Previously it has been found that similar C-layer have hole-type conductivity and a quite low layer resistance [7]. The contact from the side of n^+-GaAs substrate was formed by electrospark firing of tin foil. Current-voltage curves (IU-curves) of the produced samples were studied using a Keithley 2400 current and voltage source and meter. Spectral characteristics of photocurrent of the produced samples were investigated in the wavelength range from 0.2 to $1.5\,\mu$m using an original automated setup assembled on the basis of a MDR-23 monochromater. All the above-listed investigations were conducted at room temperature.

Table 1. Process conditions of the formation of gallium-arsenide heterostructures with a carbon film on their surface

Structure	Velocity of the CCl_4 flow, mmol/min	T_{gC}, °C	Thickness of cap layer of GaAs, nm
A	1.25	700	20
B	0.67	650	50
C	1.25	600	50
D	0.67	600	50

Note. The time of CCl_4 supply to the reactor for all structures listed in the table (time of the carbon layer formation) was 20 min.

3. Results and discussion

Structural properties of the carbon films produced by the thermal decomposition of CCl_4 were studied by Raman scattering spectroscopy. Raman scattering spectrum of the carbon layer formed at a temperature of 700°C and its approximation by Lorentz functions are shown in Fig. 1. Raman scattering spectra of C-layers produced at different temperatures are shown in the insert in Fig. 1. Parameters of fitting Lorentzians (position of the peak x_c, full width at half maximum w and area under the peak S) of the presented spectra are listed in Table 2.

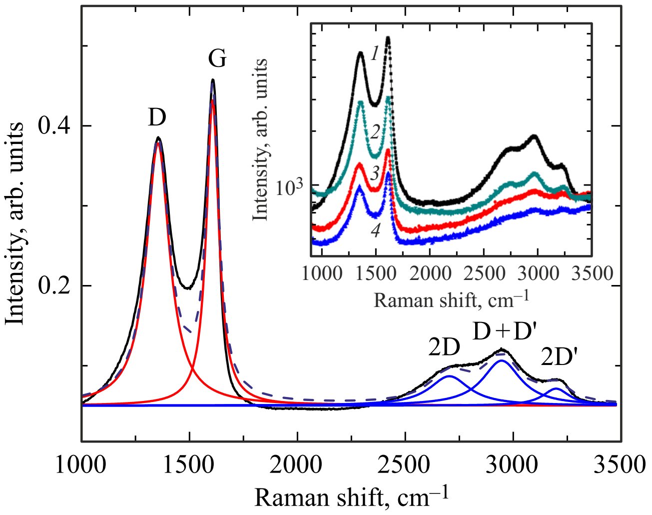

Figure 1. Raman scattering spectrum of sample A (C-layer formed at 700°C) and its fitting by peaks determined by approximation with the use of Lorentz function. The insert shows Raman scattering spectra of carbon layers for structures A (*1*), B (*2*), C (*3*) and D (*4*) (see Table 1 for process description of the structures).

Table 2. Parameters of fitting Lorentzians for samples A, B and C

Structure	Parameter	Peak D	Peak G	Peak 2D	Peak D + D’	Peak 2D’	I_{2D}/I_G	I_D/I_G	L_a, nm
A	x_c, cm^{-1}	1354	1607	2704	2946	3200	0.3	1.59	~ 7.6
	w, cm^{-1}	130	70	225	215	150			
	S	67	42	13	19	5			
B	x_c, cm^{-1}	1355	1607	2724	2950	3202	0.29	1.55	~ 8.4
	w, cm^{-1}	120	75	200	180	190			
	S	42	27	9	10	6.8			
C	x_c, cm^{-1}	1352	1608	2705	2937	3202	0.39	1.7	~ 7.1
	w, cm^{-1}	200	90	350	220	230			
	S	140	82	32	30	12			

The following peaks can be seen in Raman scattering spectrum of the high-temperature ($T_{gC} = 700°C$) carbon layer: G (near 1607 cm^{-1}) — graphite-like peak, D (at 1354 cm^{-1}) — peak caused by the presence of defects in the graphite/graphene, peaks 2D (position — 2704 cm^{-1}), D + D$'$ (at 2946 cm^{-1}) and 2D$'$ near $\sim$ 3200 cm^{-1}. The 2D band is the second-order overtone of the line D. The ratio of integral intensities of peaks D and G characterizes disordering of the carbon structure to a certain extent. It should be noted that the position of peak G is significantly shifted toward higher energies in relation to the position of the peak for single-crystal graphite of 1580 cm^{-1}. This circumstance is also indicative of the disordering in layers because in this case the shift of peak G and its broadening are probably related to the presence of the peak D$'$ at a higher energy, which also arises due to the presence of defects. With a significant disordering, peaks G and D$'$ are broaden and become hard-to-solve, therefore they are identified as a single peak G. The observed bands D, D$'$, D + D$'$ and 2D$'$ result from defects and disordering, which may arise due to the large number of edge states of the nanographite base layer and point defects [5]. The Raman scattering spectrum of the C-layer produced at $T_{gC} = 650°C$ looks similar (spectrum *2* in the insert in Fig. 1). The comparison between the observed Raman scattering spectra of the carbon layers produced by the thermal decomposition of carbon tetrachloride at temperatures of 650 and 700°C and the literature data (for example, [5,6,11,12]) shows that characteristics of the bands observed in the RS spectra and their form in general are similar to Raman scattering spectra of the vertical graphene, i.e. carbon nanostructures called carbon nanowalls [11] or nanocrystalline graphite [12] in earlier publications.

By comparing the data shown in Fig. 1 and in Table 2 to the process conditions of C-layers formation (Table 1), a trend can be seen of significant change in RS spectra with decrease in process temperature down to 600°C. In particular, a decrease in signal magnitude is observed in general, probably due to the lower thickness of the carbon film formed at 600°C (spectra *3* and *4*, insert in Fig. 1). The width at half maximum of peaks G and D increases significantly (Table 2). In addition, peaks in the region of 2D, D + D$'$ and 2D$'$ become blurred and it is difficult to distinguish them through approximation in the presence of growing background signal. All the above-listed effects are indicative of degradation of structural properties of carbon layers with decrease in the temperature of growing down to 600°C. At the same time, according to [13,14] the obtained data of Raman scattering spectroscopy allows identifying these carbon films as nanocrystalline graphite. This has been also shown by us previously in [7].

On the other hand, nanocrystalline graphite can be considered as a phase close to the multilayer graphene [13,14], i.e. it can be represented as grains of multilayer graphene. The estimating calculation of the number of layers in the multilayer graphene was carried out by the ratio of integral intensity (S) of peaks 2D and G (I_{2D}/I_G). According to [15], this value was 0.15 for the 7−8-layer graphene and 0.27 for the 4−5-layer graphene. As can be seen from Table 2, in our case A this value is equal to 0.3−0.4 and it can be assumed that it is approximately 5-layer graphene. Grain size of the multilayer graphene in the plane of layer was estimated by the following formula: $L_a = (2.4 \cdot 10^{-10}) \times \lambda^4/(I_D/I_G)$ [16], results are shown in Table 2 as well.

As it has been noted in [5,11], in the case of vertical graphene the average lateral length of nanowalls can be estimated by the value of I_D/I_G, which decreases almost linearly with increase in the lateral length of individual nanowalls [11]. It has been reported in the review [5], that such a dependence of I_D/I_G on the average lateral length of nanowalls is confirmed by many researchers and also can be explained by the above-mentioned empirical formula that describes the interrelation between plane crystallites of size L_a, the wavelength of laser source used to observe the Raman scattering and the I_D/I_G ratio. According to the

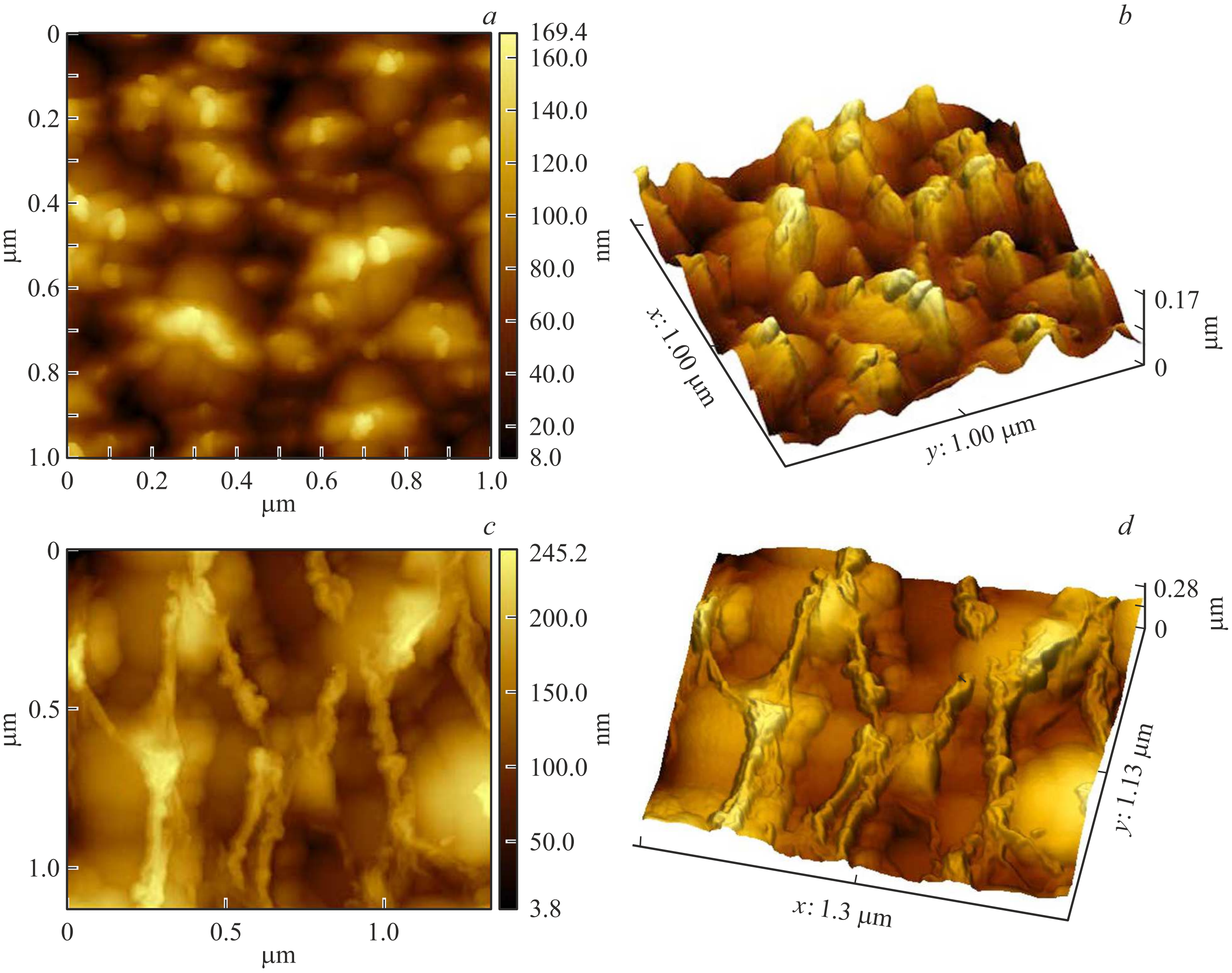

Figure 2. AFM-images of carbon layers formed at $T_{\mathrm{gC}} = 650^\circ\mathrm{C}$ (fragments *a, b*) and $T_{\mathrm{gC}} = 700^\circ\mathrm{C}$ (fragments *c, d*), on the surface of a gallium-arsenide structure.

values obtained by us, the $I_{\mathrm{D}}/I_{\mathrm{G}}$ ratio is $\sim 1.55-1.59$ for the carbon films produced by the thermal decomposition of $\mathrm{CCl_4}$ at temperatures of 650–700°C on the GaAs surface. By comparing these results to the literature data [11], it can be expected that the average lateral size of graphene nanowalls will be about 1 μm.

The results of highly sensitive AFM-studies of the surface of carbon layers produced at temperatures of 650 and 700°C are shown in Fig. 2. It can be seen that in both cases the surface of carbon film has a cellular (grain) structure, on top of cells with a size of approximately from 200 to 500 nm considerably thinner planar formations are located, which can be identified as vertical graphene. Image of the carbon film produced at a temperature of 650°C (fragments *a* and *b*) is as if the formation of vertically standing planes of graphite is just starting (their maximum height is not more than 50–70 nm). In the case of carbon layer produced at a temperature of 700°C (fragments *c, d*), the AFM-image demonstrates on top of the cellular surface more extended (in average about 1 μm) and high (about 100 nm) vertical carbon nanowalls (their thickness can be not more than 10–20 nm). As it has been found in the process of investigations, the observed vertical planes are arranged parallel to one of [110] directions of the GaAs lattice. In the case of carbon films produced at a temperature of 600°C no similar vertical nanoscale planes were observed in the AFM-image.

It has been found in the process of studies that temperature of the substrate at the decomposition of $\mathrm{CCl_4}$ has a significant effect on the optical properties of forming carbon films. Fig. 3 shows reflectance spectra of gallium-arsenide structures with a carbon film on the surface formed at a temperature of 700°C (sample A) and 600°C (sample C). Solid lines correspond to reflectance spectra taken at nearly normal incidence, dashed lines show diffuse reflectance spectra. For the case of C-layer produced at 600°C, the reflectance spectrum is completely similar to the reflectance spectrum of single-crystal GaAs; thus, it contains in the region of quantum energies from 2 to 4 eV (depth of radiation penetration is about 20 nm) a doublet of peaks,

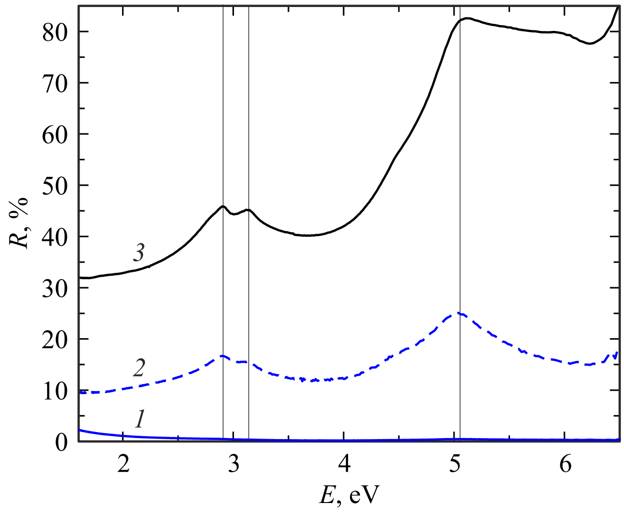

Figure 3. Reflectivity spectra of structures with a carbon film on the surface produced at nearly normal incidence of the initial radiation (solid lines 1 and 3) and diffuse reflectivity spectra (dashed line 2) in the range of radiation quantum energies in the range from 1.5 to 6.5 eV. Spectra *1* and *2* are referred to structure A, spectrum *3* corresponds to structure C.

which is typical for single-crystal GaAs in the energy range of E_1 (2.9 eV) and $E_1 + \Delta_1$ (3.12 eV) (marked by vertical lines), which corresponds to in transitions toward Λ of the Brillouin zone [17]. At the same time reflectivity coefficients within the entire spectral range also coincide with the data for smooth GaAs surface. Also, it is worth to note that the diffuse spectrum is completely coincided with the reflectance spectrum at the nearly normal incidence for sample C.

An increase in the growing temperature to 650−700°C results in a significant decrease of reflectivity coefficient at nearly normal incidence of the radiation (down to 1−10% at 700°C) throughout the entire wavelength range. Shape of the diffuse reflectivity spectrum for the sample produced at 700°C is similar to the reflectance spectrum for single-crystal GaAs but the reflectivity coefficient is not more than 25%. The observed difference in the presented spectra is indicative of a considerable radiation scattering on the rough irregularities on the surface of structure A. Also, optical characteristics of the diffuse reflectivity spectrum, on one hand, suggest the existence of a rather high-quality carbon layer/GaAs interface and, on the other hand, show an increase in the absorption of incident radiation by the structure with carbon film (vertical graphene).

Previously, it has been also shown [7] that carbon layers like these have hole-type conductivity, are rather low-ohmic, possess chemical and mechanical resistance. Therefore, the presence of the ability to increase „absorbing" capability of gallium-arsenide structures make them promising for the use as conductive contacts in photo-sensitive semiconductor devices. This is confirmed by preliminary results of studies of current-voltage curves and spectral dependencies of photocurrent for the structures with carbon film produced at 700 and 600°C (structures A and C, respectively). The produced structures demonstrate diode-type current-voltage curves (insert in Fig. 4), and in the case of structures with a high-temperature C-layer backward currents are rather low (10 μA at a bias voltage of −2 V), and the forward current increases up to 50 mA at a voltage of about 1.4 V. This is indicative of the formation of a high-quality barrier at the C-layer/GaAs interface. The shape of the current-voltage curve for the carbon film produced at 600°C shows a significant degradation of characteristics of such barrier: high backward currents and slow increase in the forward-bias current.

The obtained electrical characteristics are well correlated with photovoltaic properties of the investigated structures. It can be seen from the spectral dependencies of photocurrent shown in Fig. 4 that in the case of structure A (where the C-layer can be identified as a vertical graphene) a significant increase is observed in the signal recorded in the range of visible radiation (with wavelengths from 0.4 to 0.85 μm) as compared to the spectral dependence of photocurrent for the carbon film produced at 600°C (structure C). In addition, in the spectrum of structure A an increase in the photocurrent by two orders of magnitude is observed at wavelengths over 0.85 μm. Further investigations are required to find out mechanisms of emergence of such spectral dependencies of photocurrent in the case of structures with vertical graphene on the surface. At the same time, the obtained data makes it possible to consider such gallium-arsenide structures with a carbon film produced by thermal decomposition of carbon tetrachloride at temperatures of 650−700°C as promising candidates for the development of photo-sensitive elements (photodetectors and solar cells).

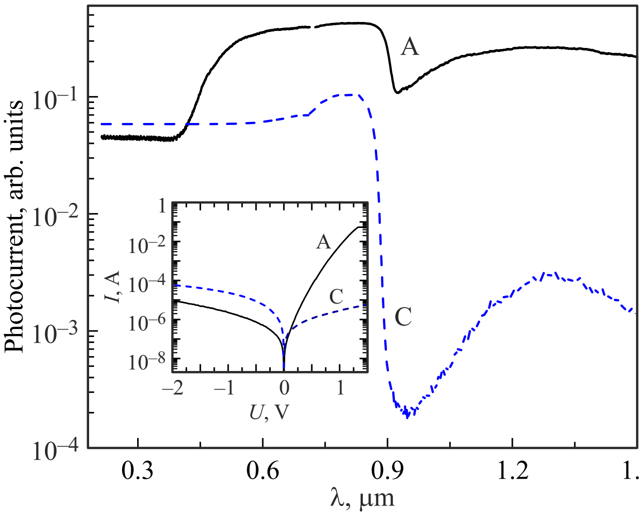

Figure 4. Spectral dependencies of photocurrent of structures A and C. The insert shows correspondent current-voltage curves. Measurements are performed at room temperature.

4. Conclusion

Thus, using the method of thermal decomposition of carbon tetrachloride in hydrogen flow carbon structures have been formed on the GaAs surface and their morphology and properties have been investigated. It has been shown by atomic-force microscopy that at temperatures of growth of 650 and 700°C an array of vertically-aligned nanolayers (vertical graphene) is formed. The studies of Raman scattering have allowed making a conclusion that these are graphite-like polycrystalline nanolayers with a grain size of about $7-8\,\text{nm}$ and the number of graphene layers in grains is about 5. Due to the developed morphology the layers have low reflectivity coefficient in the range of visible wavelengths. The C-layer/GaAs structures have rectifying properties with low backward currents and demonstrate a considerable photo-sensitivity in the wavelength range of $0.9-1.5\,\mu\text{m}$.

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Conflict of interest

The authors declare that they have no conflict of interest.

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