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Influence of Substrates on Conductivity of Thin Carbon Films Deposited by Methane Plasma and Subsequent Annealed

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Abstract. The properties of thin carbon films obtained by the deposition of carbon in CH₄ - plasma on the surface of various substrates (Si, SiO₂ and quartz glass) and subsequent annealing at 650 to 800 °C were investigated. The sizes of graphene domains from 5 to 15 nm from Raman spectra were determined which increases with rising temperature on synthesis of carbon films. Also, sizes of graphene domains were estimated based on the electrical conductivities of obtained carbon films, and their values were equal ~10.8 nm. The Efros-Shklovskii variable-range hopping (ES-VRH) conduction mechanism is replaced by percolation conductivity with increasing temperature from 650 to 800° C. When using Si substrates, the hopping mechanism was not observed at all temperatures.

1. Introduction

In recent years, interest of researchers around the world in thin carbon films has increased significantly. First of all, this is due to the possibility of obtaining two-dimensional carbon structures [1]. Such films have unique physicochemical properties and are of interest for many practical applications. Of particular interest is the use as active elements in electronic devices [2-6], and sensors [7,8].

One of the important parameters in such applications is the electrical conductivity of the material and its dependence on temperature. Mechanism of charge carrier transport is changed [9,10] with decreasing temperature in semiconductor materials. At high temperatures, temperature dependence of the resistance is determined by the thermal activation mechanism

$$R(T) = R_0 \exp(E_A / k_B T), \quad (1)$$

where R_0 - constant factor, E_A - activation energy, k_B - Boltzmann constant. With decreasing temperature, this mechanism is replaced by variable range hopping (VRH) mechanism, which is determined by Mott's law [11]:

$$\sigma = \sigma_0 \exp[-(T_0 / T)^n], \quad (2)$$

where σ_0 - preexponential factor, T_0 - characteristic temperature. Degree of the exponent is $n=(d+1)^{-1}$, where $d=1/3$ or $1/2$, depending on the spatial dimension of the sample. $n=1/2$ corresponds to the Efros-Shklovskii (ES-VRH) conduction mechanism, which takes into account the presence of the Coulomb interaction between electrons in localized states. In this case, the preexponential factor, depending on the properties of the material, is determined by the expression [12]:



$$T_o = T_{ES} = \frac{2.8e^2}{4\pi\epsilon\epsilon_0 k_B \xi} \quad (3)$$

where e is the electron charge, ϵ_0 is the electric constant, ϵ is the relative dielectric constant, ξ is the length of the localization region of the electron wave function.

It is difficult to distinguish experimentally some variants of VRH mechanism corresponding, for example, $n=1/2$ and $1/3$ via using expression (2). This requires significant changes in electrical conductivity and accurate consideration of the preexponential factor [10]. Therefore, the differential method of analysis of the Arrhenius equation for electrical conductivity, proposed in [13], used to solve this problem. According to this method, a value of n can be determined from the equation $\ln W = A - n \ln T$, where W - reduced activation energy, determined from this expression:

$$W(T) = - \frac{\partial \ln R(T)}{\partial T} = n \left(\frac{T_0}{T} \right)^n, \quad (4)$$

In carbon structures, VRH conductivity was observed at temperatures close to room temperature and lower [14-17]. In this case, the mechanisms of electrical conductivity were described both by the Mott law [14-17] and Efros-Shklovskii [18]. According to other authors, predominance of a particular type of electrical conductivity mechanism depends on the mobility of charge carriers, domain sizes, defect density [19] and temperature [15]. It should be noted that there is currently no unambiguous universally accepted opinion on this issue.

To study the electrical conductivity, we used carbon films obtained by the technique described in [20]. Preliminary studies have shown that when using SiO_2 substrates and a temperature for annealing of 650°C , a VRH conduction mechanism is observed at temperatures below 200°K [21]. The resulting materials had small graphene flakes (<2 nm) and relatively large resistances (10-100 of $\text{k}\Omega/\text{sq}$) [21]. It is possible to increase the size of graphene domains and the electrical conductivity by rise an annealing temperature. At the same time, it is possible to study the effect of the structure of a material on electrical conductivity by using substrates of varying degrees of disordering. While annealing, the structure of a substrate will have a significant effect on formation of crystalline structure of the carbon film. Thus, the aim of this work was to establish the effect of substrates on the electrical conductivity of carbon films formed at various processing temperatures.

2. Materials and methods

In this work, carbon films were synthesized by the deposition of carbon in methane (CH_4) plasma on a surface of various substrates (Si, SiO_2 , quartz glass) and subsequent annealing from 650 to 800°C for up to 45 min [11-12]. The conditions of deposition of carbon in plasma chamber on a surface of samples are shown in table 1. Reactions was carried out in the chamber pumped under to 0.0015 mbar. Processing time in plasma was up to 9 min. After plasma treatment, samples were annealed at temperatures ranging from 650 to 800°C for up to 45 min in argon atmosphere. Then, obtained films were studied by Raman spectroscopy at a wavelength of 473 nm (NTegra Spectra, NT MDT). In addition, energy dispersive X-ray spectroscopy (EDS) (INCA Energy, Oxford Instruments) and temperature dependences of the current-voltage (I-V) characteristics in a two-probe method measured in the range from 80 to 300°K .

Table 1. Conditions for synthesized thin carbon films.

Substrate (samples)	Power of plasma source [W]	Exposure time [min]	Annealing temperature [$^\circ\text{C}$]	Annealing time [min]
SiO_2	200 (13.56MHz)	6	650, 700, 750, 800	30, 45
Si	200 (13.56MHz)	6	650, 700, 750, 800	30, 45
Quartz glass	200 (13.56MHz)	6 and 9	650, 700, 750	30, 45

3. Results and discussion

The Ntegra Spectra atomic force microscope (AFM) was used to determine the thickness of the quartz/plasma-deposited film interface. Figure 1a show the threshold height at this place is around 65 nm. Measurements at other points showed values from 45 to 65 nm. The film thickness increases with rising power and exposure time of the plasma source. Figure 1b show the EDS spectra corresponding to the selected region on the surface of the carbon film on SiO₂-substrate (750 °C, 30 min). The quantitative content of the elements is shown in table 2. Carbon atoms could form bonds with oxygen during plasma deposition and when interacting with air.

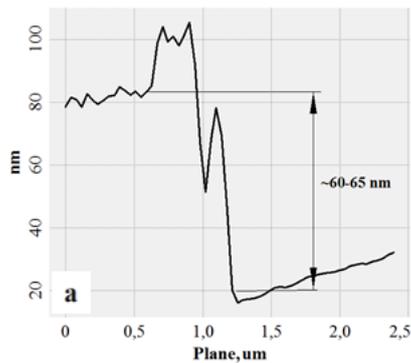


Table 2. The content of the elements in the areas “Spectra 1” in Figure 1b.

Elements	Elements content, at.
C	~85
O	~15
Si	-
Summary	100

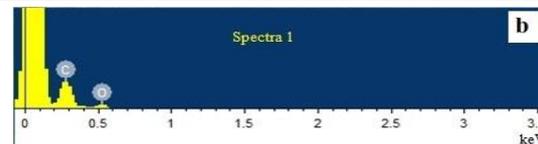


Figure 1. (a) Thickness of the quartz/plasma-deposited film interface (6 min, 750 °C); (b) EDS spectra of the sample surface after methane plasma exposure at a power of 200 W for 6 min.

Figure 2a shows graphs of the Raman spectra of samples on various substrates (750 °C, 30 min). It can be seen that D- and G-peaks are observed in the vicinity of frequencies corresponding to the typical responses of the formed graphene structures [13, 14]. As can be seen, the intensities of the G- and D-bands increase with decreasing degree of lattice disordering from amorphous quartz to crystalline silicon. It can be assumed that more honeycomb lattice forms on surface of ordered structure (G-band intensity increases) and, accordingly, number of disordering in it increases (D-band intensity increases). The integrated intensities of the bands were calculated from the obtained spectra. The calculations of the I_D/I_G - peaks ratio were carried out in accordance with the method proposed in [28]. Figure 2b shows the dependence of the I_D/I_G ratios vs substrate materials. It follows from the figure that for a crystal structure of Si this ratio is a smallest. This confirms above about a number of dependence and/or size of graphene domains in the carbon film on the structure of the substrate. Graphene domain sizes can be estimated via the I_D/I_G ratio [29]:

$$L_a (nm) = (2.4 \times 10^{-10}) \lambda_{laser}^4 \left(\frac{I_D}{I_G} \right)^{-1}, \quad (5)$$

where λ_{laser} -laser radiation wavelengths. The calculations showed that the size of graphene domains became approximately equal to ~ 5-15 nm. It should be noted that the domain sizes in Si were obtained approximately 1.5 times larger than in quartz.

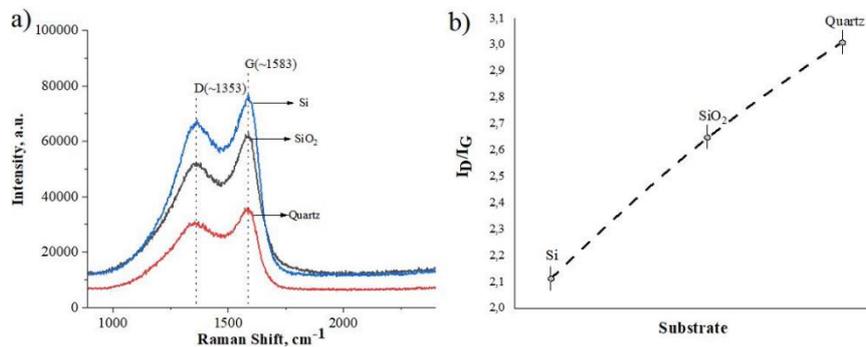


Figure 2. (a) Raman spectra of samples on various substrates under a same conditions of plasma deposition (200W, 6 min) and annealing (750 °C, 30 min); (b) dependency of the ratio of I_D and I_G – peaks depending on a substrate.

Figure 3 shows the dependences of the electrical conductivity of the samples on different substrates obtained by the two-probe method under the same annealing condition (750 °C, 45 min). Typical values of electrical conductivities are given in table 3. From the above dependence it follows that the electrical conductivity of the obtained films strongly depends on the substrate material. The lowest values were obtained for the sample on a quartz substrate. This can be explained by fact that the substrate itself is a more amorphous structure than SiO_2 and Si.

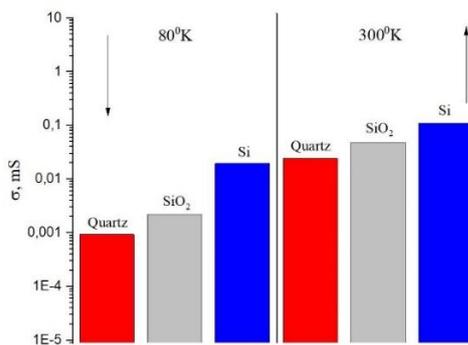


Figure 3. Values of electrical conductivities of samples on different substrates under the same annealing condition (750 °C, 45 min).

Table 3. The value of the conductivity of carbon films on various substrates at different temperatures.

T [K]	Quartz [mS]	SiO ₂ [mS]	Si [mS]
80	0.00093	0.00219	0.0194
100	0.00136	0.00379	0.0259
200	0.00954	0.01995	0.039
300	0.02433	0.047	0.109

Normalized values a conductivity of the samples based on obtained I-V characteristics were calculated. Figure 4a shows the dependences of electrical conductivity on inverse temperature for carbon films deposited on various substrates after annealing in 750°C. As can be seen, at low temperatures (80-250 °K) changes is nonlinear (non-Arrhenius). Difference is more than 2 orders of magnitude with decreasing temperature to 80 °K for quartz and SiO_2 substrates. At the same time, change in electrical conductivity on the Si substrate is only one order.

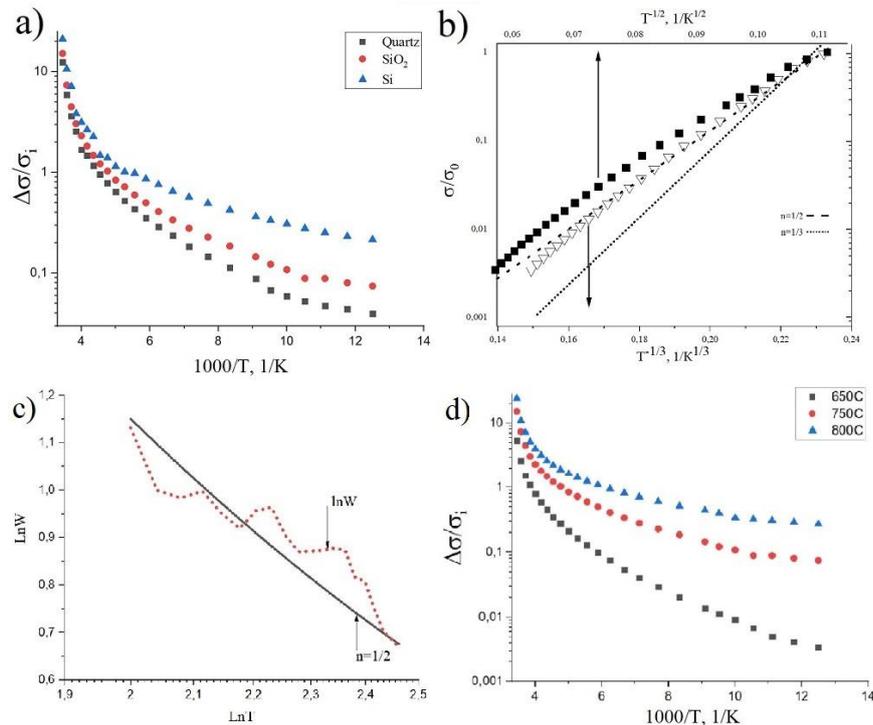


Figure 4. a) Temperature dependencies of the electrical conductivity of carbon films on various substrates after annealing of 750 °C; b) dependency of relative conductivities versus $T^{-1/2}$ and $T^{-1/3}$ for sample on the quartz substrate; c) reduced activation energy (W) of sample on a quartz substrate (700 °C, 45 min) plotted versus temperature (T) in a log-log scale; d) temperature dependencies of the electrical conductivity of carbon films on a SiO₂-substrate at various temperatures ($t = 30$ min).

The linear dependences $\sigma(T^{-1/2})$ and $\sigma(T^{-1/3})$ were obtained for samples on a quartz substrate (figure 4b). As can be seen from this figure, carbon films synthesized on Si and SiO₂ substrates also had a non-Arrhenius form. Thus, electrical conductivity of these samples is not VRH and is possibly associated with the percolation conductivity of the polycrystalline structure [30]. Thus, the results obtained made it possible to calculate VRH conductivity only for films on quartz substrates. Dependences of $\ln W$ on $\ln T$ were constructed (figure 4c) via formula (4). As can be seen from Figure 4c, the value of degree $n=1/2$ in expression (2) quite accurately corresponds to the obtained dependence.

Value of the characteristic temperature $T_0 \approx 2200$ °K was determined from the slope of $\ln T$ from $T^{-1/2}$ (figure 4c). Using by formula (3) and accepting for the value of the dielectric constant $\epsilon=4$ [25], we determined the sizes of electron localization region $\xi \approx 5.4$ nm was found. Thus, a size of the graphene domain (sp^2 -region), equal to $d \sim 2\xi$, is about 10.8 nm. These values are in good agreement with the values obtained from the I_D/I_G -ratio of the Raman peaks.

Figure 4d show the dependences of the relative conductivity of samples on SiO₂ substrates at various temperatures. As can be seen, electrical conductivity of the films strongly depends on annealing conditions. The change in conductivity exceeds 3 orders of magnitude for samples treated at a temperature of 650°C. At the same time, for samples processed at 800 °C, difference is less than one order of magnitude. Thus, VRH conductivity, which was observed at $T=650$ °C [20,21], is not observed with an increase in the synthesis temperature of samples to 750°C.

4. Conclusion

The properties of thin carbon films obtained by deposition of carbon in a methane plasma and subsequently annealed at temperatures from 650 to 800 °C were studied. Analysis of the Raman spectra showed that for the samples obtained, the ratio of intensities I_D/I_G depends on the degree of ordering of the substrate structure. The sizes of graphene domains from 5 to 15 nm were determined from Raman

spectra. The sizes of graphene domains on a silicon substrate are approximately 1.5 times larger than on quartz glass.

The electrical conductivity of the obtained films strongly depends on annealing conditions and a substrate material. The hopping conductivity at $T > 650$ °C was investigated only for samples on a quartz substrate. It was also observed for samples on SiO₂ substrates at temperature $T = 650$ °C. It was found that an electrical conductivity mechanism corresponds to the Efros-Shklovskii VRH mechanism law for localized states in graphene domains from based on measurements of the temperature dependences of the electrical conductivities for films synthesized on a quartz substrate at $T = 750$ °C. Thus, a size of graphene domains ($d \sim 10.8$ nm) was obtained. These values are approximately 5 times larger than the domain sizes obtained for samples synthesized on a SiO₂ substrate at $T = 650$ °C. The results obtained suggest that the use of ordered crystalline structures as substrates for a synthesis of carbon films by deposition of carbon in CH₄-plasma and subsequent annealing lead to an increase in the size of the formed graphene domains. A similar increase occurs with an increase in the synthesis temperature from 650 °C and higher. The rise in a size of domains leads to a change in the mechanism of electrical conductivity from hopping to percolation or thermal activation.

Acknowledgments

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References

- [1] Novoselov K S, Geim A K, Morozov S V, Jiang D, Zhang Y, Dubonos S V, I. Grigorieva V and Firsov A A 2004 *Science* **306** 666-669
- [2] Sang M, Shin J, Kim K and Yu J K 2019 *Nanomaterials* **9**(3) 374
- [3] Zhan B, Li C, Yang J, Jenkins G, Huang W and Dong X 2014 *Small* **10**(20) 4042-4065
- [4] Avouris P, Freitag M 2013 *IEEE Journal of selected topics in quantum electronics* **20**(1) 72-83
- [5] Bonaccorso F, Sun Z, Hasan T and Ferrari A C 2010 *Nature photonics* **4**(9) 611
- [6] Bablich A, Kataria S and Lemme M C 2016 *Electronics* **5**(1) 13
- [7] Nag A, Mitra A and Mukhopadhyay S C 2018 *Sensors and Actuators A: Physical* **270** 177-194
- [8] Huang H, Su S, Wu N, Wan H, Wan S, Bi H and Sun L 2019 *Frontiers in chemistry* **7**
- [9] Shklovskii B I, Efros A L 1975 *Uspehi fizicheskikh nauk* **117**(11) 401-435
- [10] Gantmaher V F 2013 *Electrons in disordered media Moscow* (in Russian) 288
- [11] Mott N F, Davis E A, *Electronic Processes in Non-Crystalline Materials Oxford: Clarendon*
- [12] Joung D, Khondaker S I 2014 *Physical Review* **89** 245411 1-6
- [13] Zabrodskii A and Zinoveva K 1984 *Zh. Eksp. Teor. Fiz.* **86** 742
- [14] Gómez-Navarro C, Weitz R T, Bittner R T, Scolari X, Mews A, Burghard M and Kern K 2007 *Nano letters* **7** (11) 3499-3503
- [15] Park M, Hong S J, Kim K H, Kang H, Lee M, Jeong D H, Park Y W, Kim B H 2017 *Applied Physics Letters* **111** (17) 173103
- [16] Kaiser A B, Gómez-Navarro C, Sundaram R S, Burghard M and Kern K 2009 *Nano letters* **9** (5) 1787-1792
- [17] Kumar R, Kaur A 2015 *IET Circuits, Devices & Systems* **9**, 392-396
- [18] Joung D, Khondaker S I 2012 *Physical Review B* **86** 235423 1-8
- [19] Haque A, Abdullah-Ali M, Mamun, M F, Taufique N, Karnati P, Ghosh K 2018 *IEEE Transactions on Semiconductor Manufacturing* **31** 535-544
- [20] Neustroev E P, Popov V I, Prokopiev A R, Davydova Z Y, and Semenov S O 2019 *AIP Conference Proceedings* **2179** 020019
- [21] Neustroev E P, Prokopiev A R 2019 *Radioelectronics. Nanosystems. Information Technologies* **11** – 315-320
- [22] Neustroev E P, Prokopiev A R, Timofeev V B, Popov V I, Kurkina I I, Davydova Z Y, Alekseev A A and Semenov S O 2019 *IOP Conf. Ser.: Mater. Sci. Eng.* **693** 012043
- [23] Mohan V B, Nieuwoudt M, Jayaraman K, et al 2017 *Graphene Technol* **2** 47–62

- [24] Pawbake A S, Mishra K K, Machuno L G B, Gelamo R V, Ravindran T R, Rout C S and Late D 2018 *J. Diamond and Related Materials* **84** 146–156
- [25] Ferrari A C and Basko D M 2013 *Nature nanotechnology* **8** 235
- [26] Beams R, Caçado L G and Novotny L 2015 *Journal of Physics: Condensed Matter* **27** 083002
- [27] Nekrashevich S S, Gritsenko V A 2014 *Physics of the Solid State* **56** 207-222
- [28] Dresselhaus M S, Jorio A, Souza A G Filho and Saito R 2010 *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences* **368** 5355-5377
- [29] Jorio A, Ferreira E H M, Moutinho M V O, Stavale F, Achete C A and Capaz R B 2010 *Phys. Status Solidi B* **247** 2980–2982
- [30] Sun L H, Ounaies Z, Gao X L, Whalen C A, Yang Z G 2010 *Journal of Nanomaterials* **2011**