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STUDY OF THE STRUCTURE OF AMORPHOUS CARBON FILMS MODIFIED WITH SILICON OXIDE

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This paper considers amorphous carbon films modified with silicon oxide (a-C_{1-x}:$(SiO)_x$),obtained by the method of magnetron ion-plasma co-sputtering of a combined target in an argon atmosphere. The topography and phase contrast of the film surface were studied by atomic force microscopy. The local structure was studied by Raman spectroscopy. It is shown that an increase in the concentration of silicon leads to an increase in the intensity of photoluminescence. The shift of the G peak to the low-frequency region in a-C_{1-x}:$(SiO)_x$ films indicates an increase in the sp^3 hybridization of carbon bonds.

***Keywords*:** silicon containing amorphous carbon films, atomic force microscopy, Raman spectroscopy, photoluminescence, bond hybridization.

Introduction

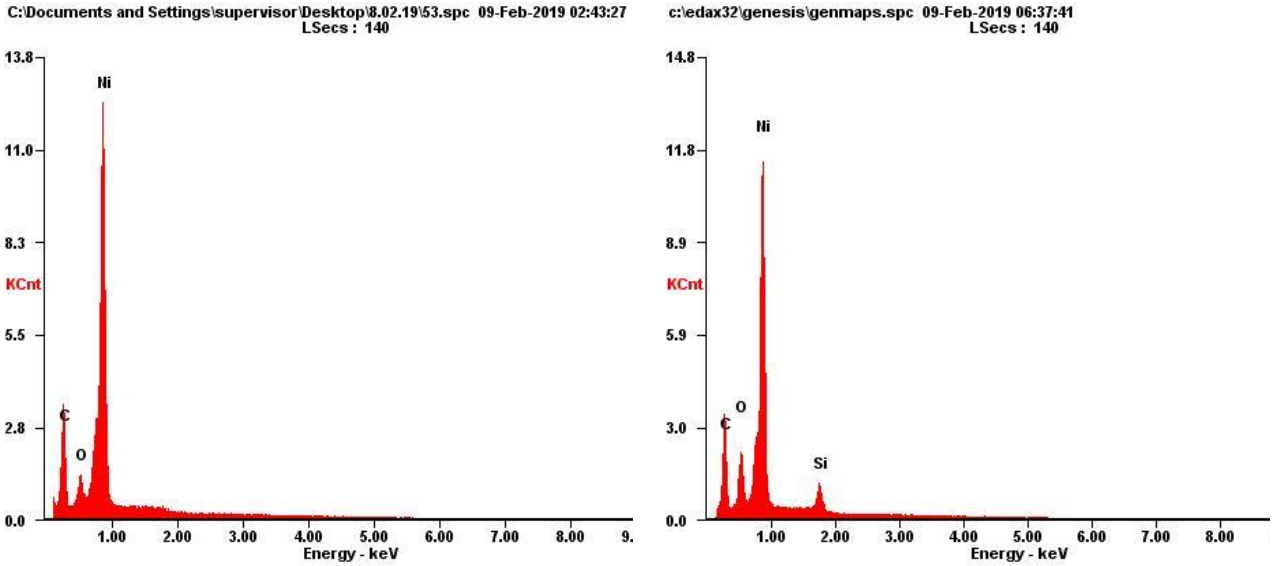
Recently, interest in silicon carbide films as a promising material for nanoelectronics and photonics has increased. Moreover, amorphous carbon films modified with silicon and oxygen atoms are of no small interest. Therefore, studies of thin amorphous carbon films modified with structural units of silicon oxide with concentrations up to 20 at. % can reveal new properties.

a-C_{1-x}:$(SiO)_x$ films can have unique properties such as high chemical resistance and high mechanical strength, and resistance to external actions (radiation, temperature, etc.). SiO-doped modified carbon films are classified as wide bandgap semiconductor and may be promising for the development and creation of new semiconductor devices and appliances in the terahertz frequency range. Silicon carbide can form various modifications of the structure, the main of which are 3C (face-centered cubic), 4H and 6H (hexagonal structures) [1]. These structures have individual electronic properties. Therefore, one of the important issues is the possibility of controlling the electronic properties of amorphous carbon films by structural elements of 3C, 4H and 6H groups. The introduction of oxidized structural units into an amorphous carbon matrix should lead to a significant change in the structure and properties of the synthesized carbon films. Knowledge of the effect of synthesis conditions on the formation of a structure with a certain ratio of polymorphic structural units will allow to manage and control electronic processes in thin films of amorphous carbon more effectively. This will make it possible to obtain structurally modified a-C:SiO films with desired properties.

1. Experimental part

Synthesis of nanostructured nanoscale a-C:SiO films was carried out by the method of magnetron ion-plasma co-sputtering of a combined carbon target (99.999 at.%) and high-resistance silicon (100) (~200 МОm/см^3) at a direct current in argon atmosphere (99.999 at. %). a-C_{1-x}:$(SiO)_x$ films were simultaneously deposited on quartz, silicon and nickel substrates for 45 minutes with an average growth rate of 3.3 nm/min. The power of the ion-plasma discharge was 14 Watts. The temperature of the synthesized films did not exceed 50°C; the argon pressure was constant and was equal to 0.7 Pa. The thickness of all the films obtained varied from 50 to 100 nm.

The concentration of silicon and oxygen was determined by the method of energy dispersive spectroscopy (EDS) analysis using Quanta 200i 3D scanning electron microscope (FEI Company, USA) in films synthesized on a nickel polished substrate (Fig. 1). Nickel is the only metal the EDS signal of which does not intersect with spectra from carbon, silicon, and oxygen.



a b

Fig.1. EDS spectra obtained from a) a-C film; b) a-C_{1-x}:$(SiO)_x$film synthesized on nickel substrate.

In addition, it can be seen that the EDS spectra of other elements were not detected in the synthesized films. The increasing concentration of silicon leads to an increase in oxygen. The thickness of the films was determined on the fresh cleavage of a silicon wafer, as shown in Fig. 2.

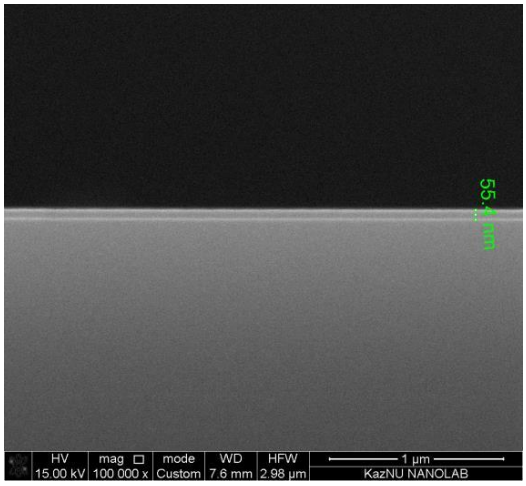


Fig.2. Examples of thickness measurements of a-C_{1-x}:$(SiO)_x$ film

The relative silicon concentration in the amorphous carbon film was calculated without taking into account the oxygen concentration, Table 1. An increase in the EDS peak from oxygen depends both on its presence on the surface of the nickel plate (before the synthesis), and on the surface of the film after taking it out the chamber. In addition, the intensity of the EDS peak of oxygen will be affected by x-rays from nickel atoms. Therefore, taking oxygen into account in calculating the relative concentration would not be correct.

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Table 1. The relative silicon concentration in the amorphous carbon film.

Sample Number	1	2	3	4	5	6	7	8	9
$X=X_{Si}/(X_C+X_{Si})$	0	0.04	0.051	0.06	0.07	0.10	0.11	0.12	0.162

Surface topography and phase contrast of the films were studied using atomic-force microscope of Solver Spectrum instrument (NT-MDT, Russia). In addition, the local structure was studied by the Raman spectroscopy method using a NTegra Spectra spectrometer (NT-MDT, Russia).

2. Results and discussions

Topography and phase contrast of the a-C_{1-x}:$(SiO)_x$ films were studied by the method of semi-contact atomic force microscopy. The measurements were carried out using an NSG-01 probe with a radius of less than 10 nm and oscillation frequency of ~190 kHz. Fig. 3 (a, c, e) shows the topography of film surface with a relative concentration of silicon in the carbon film being 0, 0.05, 0.16. As can be seen from the figure, the size of the globules forming the film structure increases with increasing concentration of silicon oxide. Figure 3 (b, d, f) shows the phase contrast of the surface; this method of research in atomic-force microscopy shows the existence of regions with different electron density, which would indicate the difference in the phase state of the synthesized films' structure.

Fig. 3 demonstrates that the surface topography patterns of the films with different concentrations of silicon and oxygen are significantly different, but the changes in the phase of probe oscillations are not sufficient (Fig. 3 b, d, f), which can be explained by a change in the surface relief pattern, rather than structural characteristics. Thus, the absence of significant contrast over the entire surface indicates the uniform distribution of electron density over the surface of the synthesized films. Thus, formation of separate structural fragments of silicon and oxygen atoms is absent. The structure primarily forms from carbon and silicon atoms, while oxygen atoms participate as a link between the Si-C and Si-Si structural units.

In confirmation of the above, the local structure of the synthesized films was studied using Raman spectroscopy at an excitation wavelength of 473 nm. Fig. 4 shows a typical Raman spectrum obtained from a-C film. In addition, it can be seen that with increasing concentration of silicon oxide there is an increase in photoluminescence. This is due to the increase in the band gap and concentration of sp^2C-C bonds [2], which determine the state of the electrons. The π bound and π^* of unbound electron states are responsible for the development of density of allowed states in the top of the valence band and the bottom of the conduction band, respectively. An increase in the formation of sp^2 hybridized bonds and an increase in the energy gap between $\pi - \pi^*$ electron states can involve both silicon and oxygen atoms, which is shown in Fig. 4 as an increase in the slope of the Raman spectrum. As is known [3], it is $\pi - \pi^*$ electronic transitions that are responsible for the appearance of photoluminescence in amorphous carbon, an increase in their concentration results in an increase in photoluminescence. Moreover, an increase in the silicon concentration leads to a shift of the main G peak to the low-frequency region, as shown in Fig. 5.

Figure 5 shows the Raman spectra minus background and photoluminescence. A typical Raman spectrum of amorphous carbon consists of a G peak and a shoulder in the low-frequency region from the main peak; in addition, we observe a second order at a frequency of 3000 cm^{-1}. G peak characterizes stretching of C-C bonds. The appearance of a shoulder in the low-frequency region indicates amorphization of the structure and characterizes the breathing mode of a hexagon molecule of carbon atoms, which is denoted by the D peak [4]. An increase in silicon oxide concentration in a-C film results in disappearance of the shoulder, i.e. D peak.

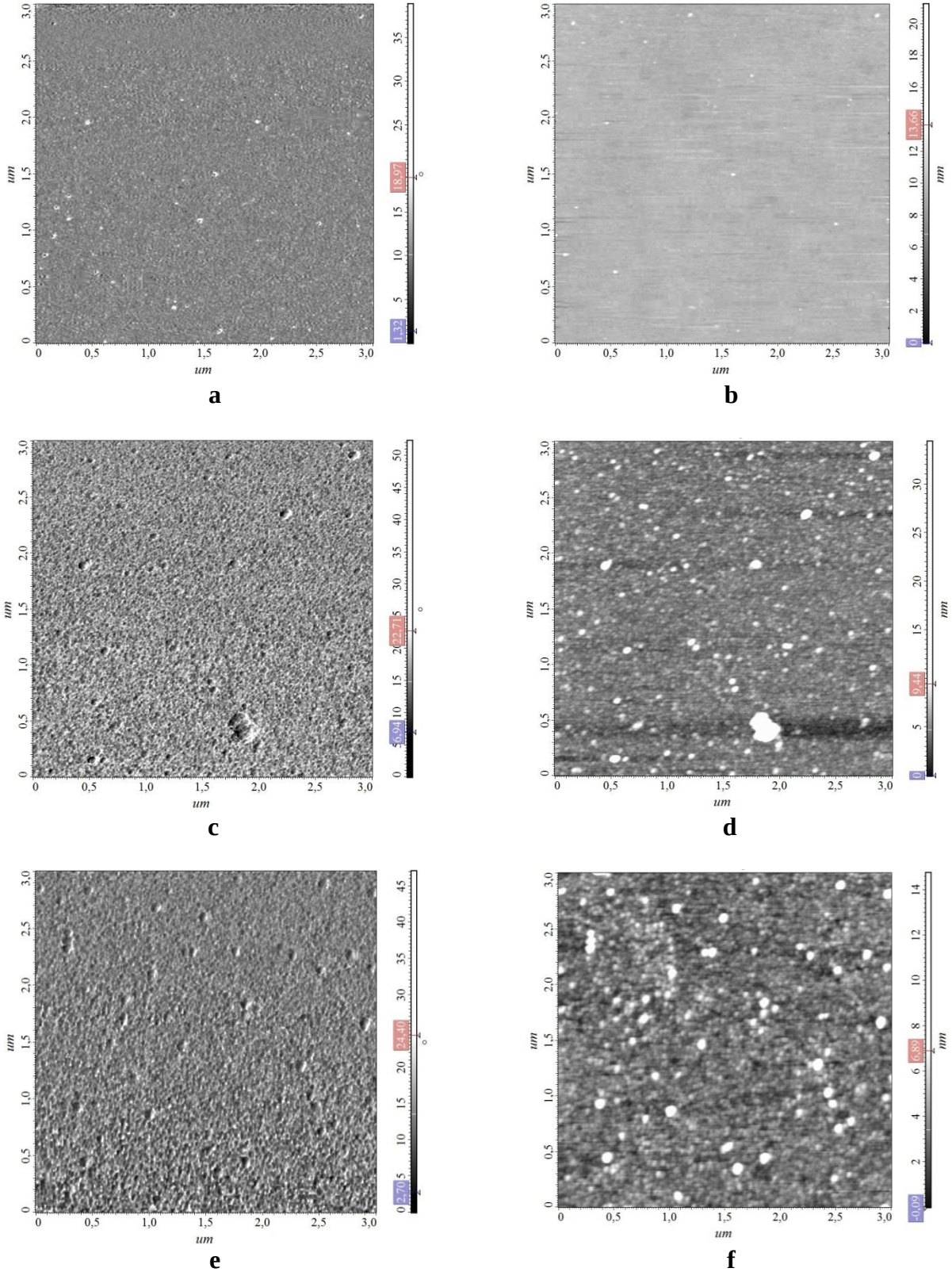

Fig. 3. AFM of a-Canda-C_{1-x}:$(SiO)_x$ films surface with relative silicon concentration in the carbon film 0; 0.051; 0.162:
a, c, e) the surface topography of the films; b, d, f) the phase contrast of the film surface

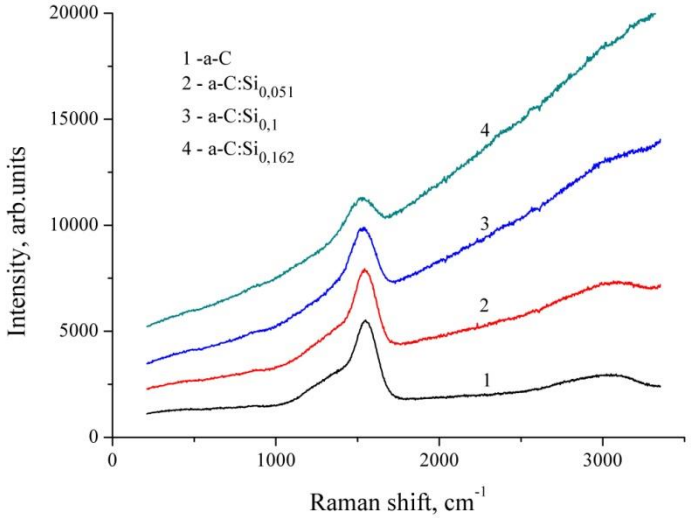

Fig. 4. Raman Spectra from a-C and a-C_x:$(SiO)_{1-x}$ films.

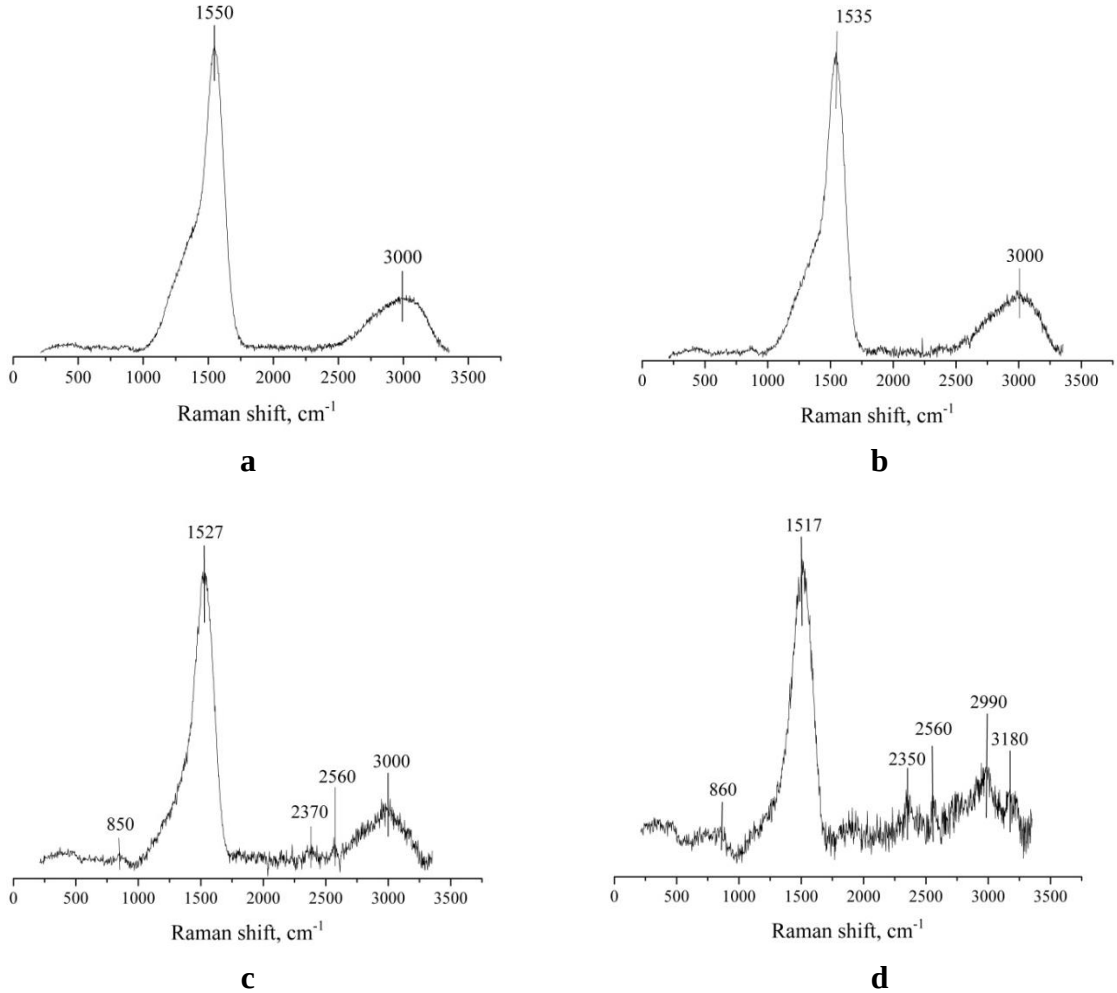

Fig. 5. Raman scattering spectraofa-C_x:$(SiO)_{1-x}$ films:
a) X_{Si}=0.0 at.%; b) X_{Si}=0.051 at.%; c) X_{Si}=0.1at.%; d) X_{Si}=0.162 at.%

This is due to the disappearance of the graphite phase and the transition to a four-coordinated bond of carbon atoms or sp^3 hybridization. At the same time, it should be noted that the appearance of some features within the frequency range of 250 cm^{-1} and 860 cm^{-1} is determined by Si-C bonds and the G peak shift to the low-frequency region of the Raman spectrum also indicates an increase in sp^3 hybridized bonds [5]. As is shown in the work [6], the G band shift to the low-frequency region indicates an increase of sp^3 hybridized bonds in the structure of carbon films. This is apparently due to the occurrence of silicon atoms, which form structures with the carbon atoms of 3C, 4H and 6H. In addition, in the high-frequency region (Fig. 5 c), we observe separation of the second order into a series of frequencies that characterize certain frequencies of bonds with carbon atoms. Apparently, this is due to the presence of silicon atoms in the lattice structure, which in a certain way affect the frequency range of the second-order phonon mode of C-C bonds.

Conclusion

It follows from the above that the surface topography of the synthesized films of amorphous carbon significantly depends on silicon oxide concentration. The study of the films' surface by the phase contrast method in atomic force microscopy had shown a uniform distribution of the structure of C-C, Si-Si, Si-C bonds making up the film. The absence of significant phase contrast indicates the uniform distribution of electron density, and therefore, the absence of the structural SiO_2units. This means that there is no formation of individual fragments of the silicon and oxygen atoms structure. The structure formation primarily comes from carbon and silicon atoms, while oxygen atoms participate as a link between the structural units of Si-C and Si-Si atoms.

Raman spectroscopy has shown that an increase in the concentration of silicon leads to an increase in photoluminescence. First of all, this is due to the increase in the width of the band gap and concentration of π-electrons.

In addition, it was found that with an increase in the silicon concentration, G peak shifts to the low-frequency region and this indicates an increase in sp^3 carbon atoms. The appearance of carbon atoms in the high-frequency region of second-order peaks is associated with the presence of silicon atoms.

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