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STRUCTURAL PECULIARITIES OF AMORPHOUS CARBON FILMS SYNTHESIZED IN AR ATMOSPHERE BY ION-PLASMA METHOD

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In this work we perform the results of complex study of thin amorphous carbon films, produced by strongly non-equilibrium method of DC magnetron ion-plasma sputtering in Ar atmosphere. In the result of performed atomic force microscopy was revealed that structure and morphology of a-C films' surface depend on gas pressure, power of plasma discharge and temperature of substrate. The basis of films' structure is globular formations of 20-100 nm depending on the synthesis conditions. Analysis of obtained films using Raman spectroscopy also shows dependence of local structure, particularly percentage of sp3 hybridized carbon bonds, on synthesis conditions. Using optical spectra of transmission and reflection, energy band gap of carbon films was calculated, and it depends on substrate temperature.

Keywords: carbon films, ion-plasma sputtering, Raman spectroscopy, morphology, atomic-force microscopy

Introduction

As it is known [1] carbon can exist in several allotropic crystalline states, such as graphite, diamond, lonsdalite, carbyne, fullerene, carbon nanotubes, etc. There are many allotropic states in an amorphous phase, such as anthracite, coke, glassy carbon, soot. These states of carbon are characterized by peculiarity of atomic structure and different physical properties. In the last decade special attention of scientists is attracted by thin amorphous carbon films (a-C). Owing to peculiarity of the synthesis of carbon films the local structure of the films may contain various forms of atomic structure from graphite-like to diamond-like and change electronic (electric, photovoltaic and optical) properties in a wide range.

There are many different methods of carbon films' synthesis aimed at the creation of certain coatings resistant to chemical attack with improved tribological and other characteristics [2]. It pays special attention to DC magnetron ion-plasma sputtering in Ar atmosphere. This method refers to strongly non-equilibrium processes and therefore has several advantages over other methods of synthesis of carbon films with disordered structure. Varying the synthesis conditions it is possible to control formation of atomic structure and, consequently, electronic properties.

1. Experimental part

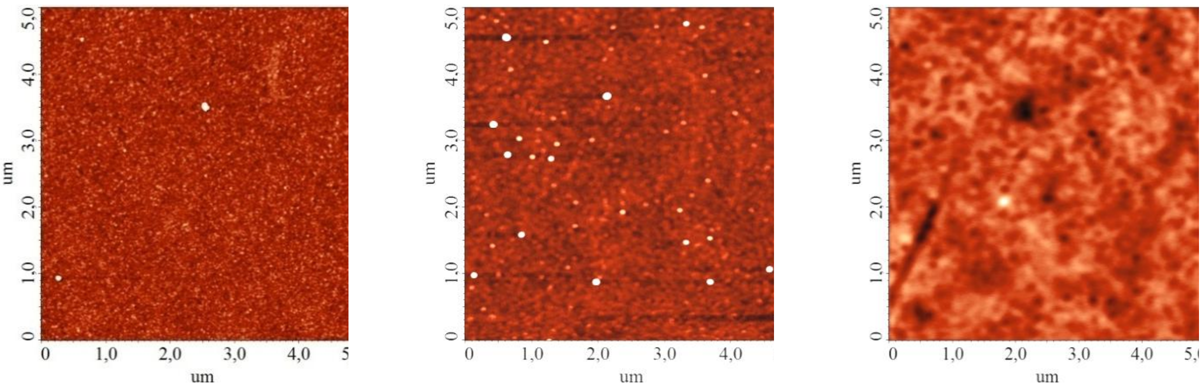
For synthesis of carbon films we used cooled magnetron with controlled variable magnetic field and with unbalanced plasma. The DC power voltage and electron-ion current in the plasma discharge were additionally adjusted by changing magnetic field during the synthesis process. Specific power of ion-plasma discharge possesses the values of 2.5 W/cm^2, 2.75 W/cm^2 and 3.0 W/cm^2. The carbon films growth was performed at three temperatures of 50, 150 and 250°C and at the gas pressures in the range from 0.5 to 1.2 Pa on glass substrates. The average rate of the films growth was about 15 Å/min.

Study of structure and surface morphology of a-C films was performed using semi-contact mode of atomic force scanning microscope NTegra Therma (NT-MDT, Russia). The local atomic structure was analyzed by Raman spectrometer NTegra Spectra (NT-MDT, Russia) with an accuracy of ± 4 cm^{-1}. Optical transmission (T) and reflectance (R) spectra were investigated using UV-3600 spectrophotometer (Shimadzu, Japan).

To study the surface morphology using an atomic force microscope force modulation technique was used. It is mostly used to characterize local mechanical properties of the samples [3]. The difference of this AFM method from the others consists of the vertical periodic oscillations of scanner within the method of constant force. As a result of the oscillation, modulation amplitude of cantilever varies depending on the elastic properties of the sample surface and the Van der Waals interaction between the sample surface and the surface of the probe with curvature radius 10 nm.

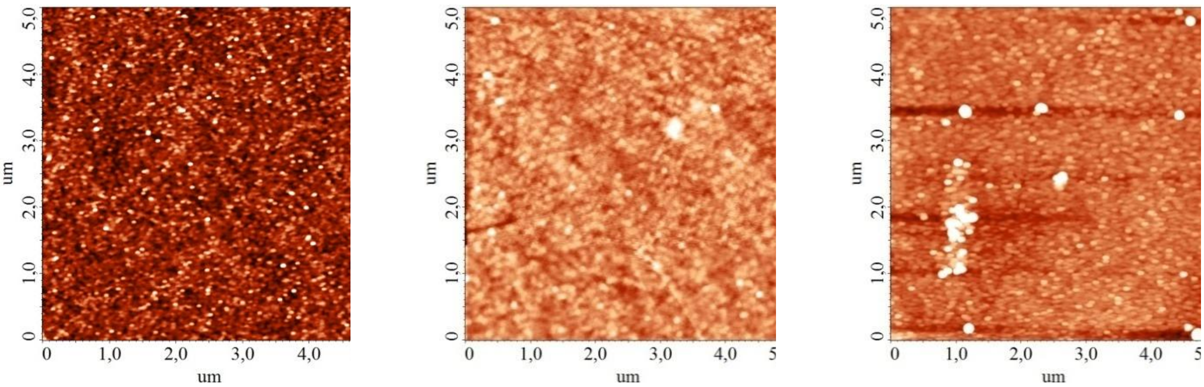
2. Results and discussion

The most characteristic regularities of AFM of synthesized amorphous carbon films were considered. Comparing the experimental results of atomic force microscopy (Figures 1, 2, 3) it can be concluded that the structure and surface morphology of the synthesized films depend on the gas pressure, the power of the plasma discharge, and strongly depend on the substrate temperature. The basis of structure of all the films is the globules from 20 to 100 nm depending on the synthesis conditions. Globule size substantially depends on thermodynamic parameters of synthesis. Globules with sizes of about 20 nm are observed in the films obtained at ion-plasma discharge power of 2.5W/cm^2 (Figure 1a) at argon pressure of 0.5 Pa and at substrate temperature of 50°C. Increase of globules size depends on such physical quantities as specific power of discharge (Figure 1) and the temperature of the substrate (Figure 2).



a) w=2.5 W/cm^2 b) w=2.75 W/cm^2 c) w=3.0 W/cm^2

Fig.1. AFM of a-C: H films surface synthesized at different values of specific power of plasma discharge, substrate temperature T_{sub}=50°C and constant pressure p=0.5 Pa

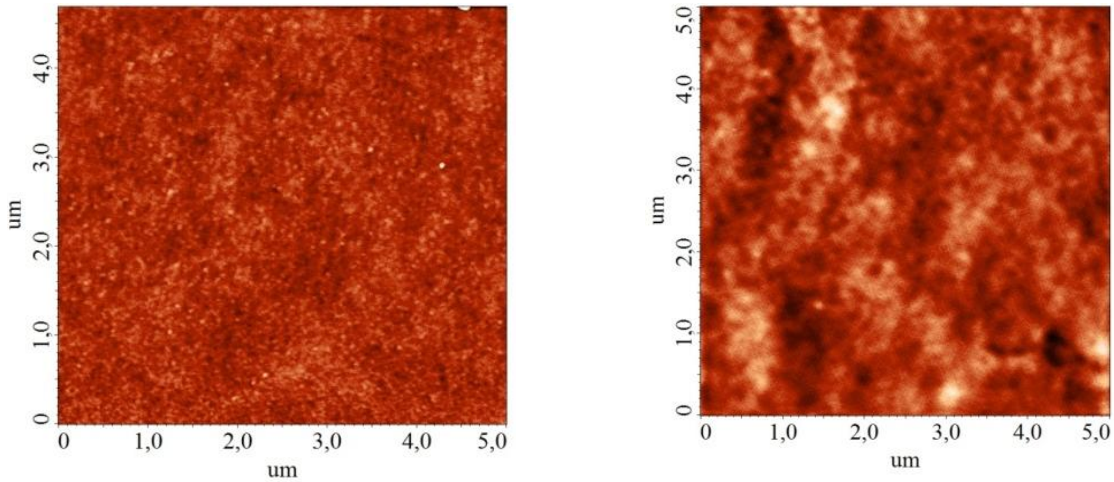


a) T=50°C b) T=150°C c) T=250°C

Fig.2. AFM of a-C:H films surface synthesized at different substrate temperatures, constant pressure p=1.2 Pa of Ar in plasma and specific power of plasma discharge w =2.75 W/cm^2

In figure 2c it is clearly seen the formation of globular cluster at a temperature of 250°C. Besides, comparing Figures 1b and 2a it can be said that the pressure of argon in the plasma also affects the formation of the structure and morphology of the surface of a-C films. Therefore we can conclude that external physical quantities influence on the atomic-molecular energy state of forming structure. Energy state of the system determines the formation of globules and clusters of certain sizes [4].

It should be noticed that the surface morphology is substantially sensitive to the changes of gas pressure in plasma at a synthesis temperature of 250°C. As shown in Figure 3 at the discharge power of 2.5 W/cm^2 and the synthesis temperature of 250°C at a pressure of 0.5 Pa the surface relief hasn't any significant roughness and consists of globules with size of ~ 20 nm and smaller. At the Ar pressure of 1.2 Pa, the energy of condensed atoms and particles is essentially changes during the synthesis process and at substrate temperature of 250°C leads to more strong iterations between the globules and further formation of large clusters. This is the cause of evident changes in height of the surface relief of the synthesized carbon film.



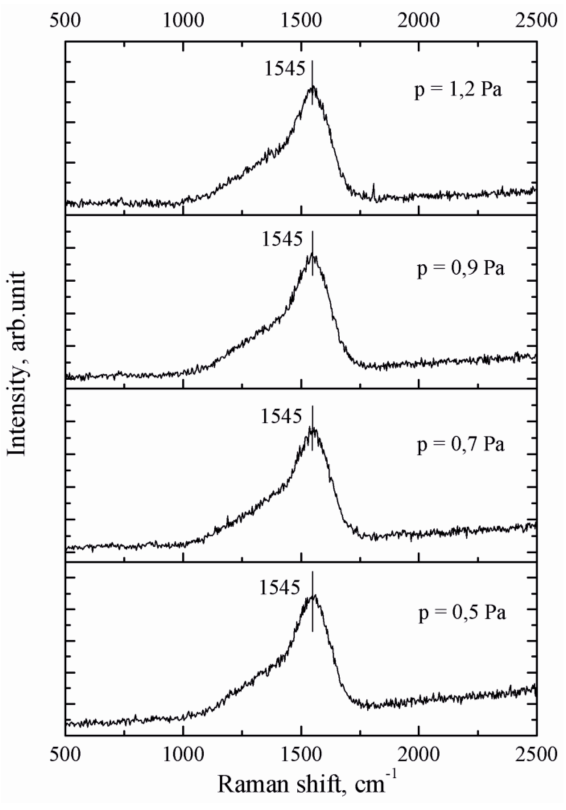
a) p=0.5 Pa b) p=1.2 Pa

Fig.3. AFM of surface of a-C:H films synthesized at different pressures of Ar, constant substrate temperatures T_{sub} =250°C and specific power of plasma discharge w = 2.5 W/cm^2

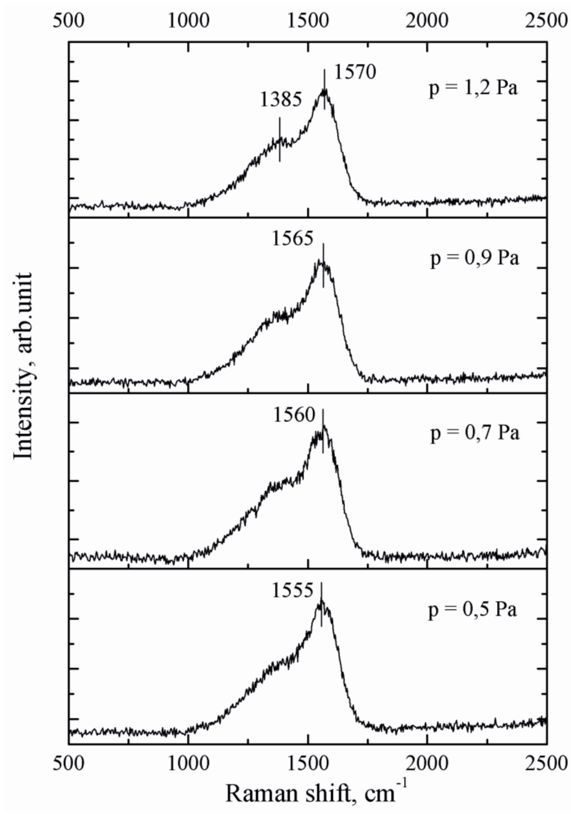
In order to study the local structure of thin amorphous carbon films Raman spectroscopy study was performed. The structure of amorphous carbon is mainly characterized by three types of carbon bonds determined by their hybridization, such as sp^1, sp^2 and sp^3. Therefore, the structure of amorphous carbon will widely vary from polymer-like to graphite-like structure and further to diamond-like structure. The ratio of hybridization of atomic bonds in the structure will determine the properties of amorphous carbon.

Raman spectra of amorphous carbon films are described by one or two main peaks determined by the structure of the films. By the ratio of peaks intensity one can calculate the fraction of sp^2 to sp^3 bonds in the carbon matrix. The main peaks in Raman spectroscopy denoted as G (graphite) and D (disordered). The position of G peak is caused by the appearance of regions with medium range order of atomic structure within amorphous matrix. These regions are determined by oscillation processes that involve stretching and compression modes of hexagonal rings C_6.

Figure 4 shows Raman spectra of amorphous carbon films synthesized at power density of plasma discharge w = 2.5 W/cm^2 and at the temperature of 50 and 250°C. As shown in Figure 4a, there are no any substantial differences between spectra of films obtained at various argon pressures. The position of the main G peak is constant and located at 1545 cm^{-1}. It is known that in case of G peak position equal 1550 cm^{-1} and less atomic structure of amorphous carbon is mainly characterized by sp^3 bonds, with percentage of 85%. But we have to take into account that the dispersion of G peak must be about ~0.35 cm^{-1}/nm [5]. The essential difference in the Raman spectra depending on the gas pressure can be seen in a-C films synthesized at a substrate temperature of 250°C (Figure 4b). With increase of Ar pressure position of G peak is shifted toward the higher energies to the value of 1580 cm^{-1}, which characterizes the main band of pyrolytic graphite. I.e. we can conclude that the concentration of sp^2 hybridized bonds as well as the number of hexagonal rings C_6 increase. Increase of the number of C_6 rings is proved by the increase of D band, which is manifested as the shoulder in the low-frequency region of G band. The D peak appears in graphite only in case of emergence of additional degree of freedom in the hexagonal molecule consisted of carbon atoms, which leads to the breathing mode in C_6. As it seen in Figure 4b at a gas pressure p = 1.2 Pa pronounced peak D at 1385 cm^{-1} is observed. Increase of the pressure of working gas leads to decrease of energy of condensation, resulting in the formation mainly sp^2 hybridized bonds, and substrate temperature additionally promotes this process. Thus the formation of graphite-like structural units is observed. As noted in [1], nanoparticles with size greater than 1 nm are mainly formed from structural units of sp^2 sites and C_6 molecules. It should be noted that globules can consist either of sp^2 and sp^3 sites forming graphite-like or polymer-like structures respectively. G peak possesses the value of 1550 cm^{-1} for all a-C films synthesized at different argon pressure, the substrate temperature of 150°C and sputtering power density of 2.5 W/cm^2.



a)

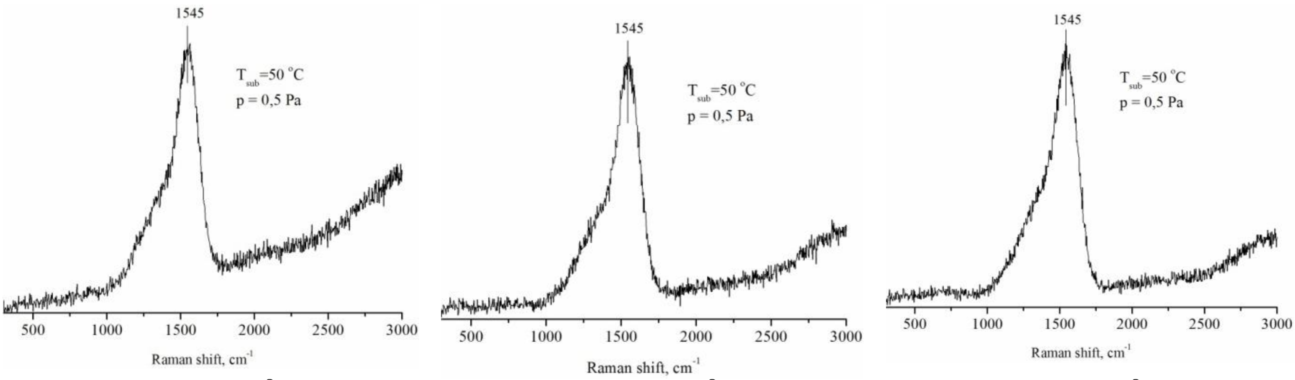


b)

Fig.4. Raman spectra of a-C films synthesized at a) 50°C, b) 250°C and at sputtering power density of 2.5 W/cm^2

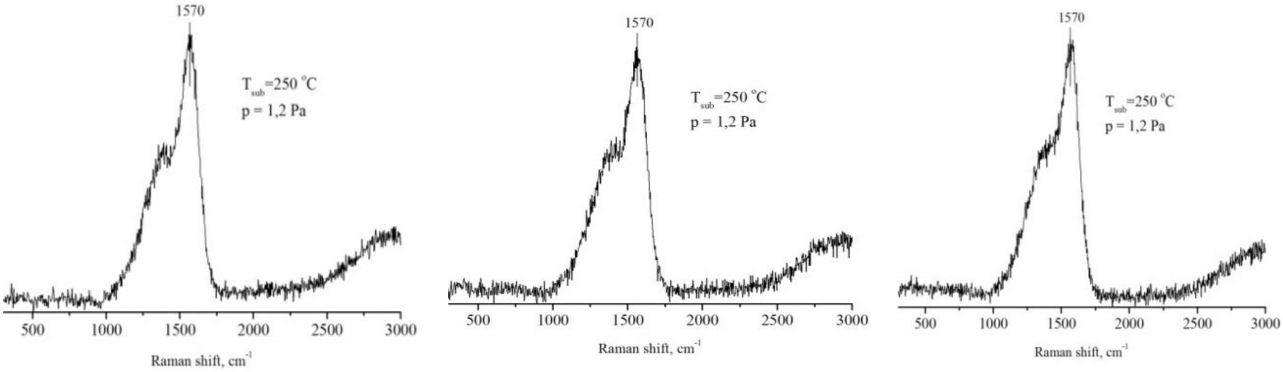
Figure 5 shows Raman spectra of amorphous carbon films synthesized at different power density and at the same Ar pressure and substrate temperature. It can be seen that the power of plasma discharge doesn't affect on the structure formation as the position of the main G band is constant and remains at 1545 cm-1. The shape of the spectrum is essentially the same but there is a difference expressed in changing the slope of the spectrum in the high frequency region, which characterizes the appearance of the luminescence. Increase the power of plasma discharge results in a decrease of slope in high frequency region, which indicates a decrease of luminescence. This in turn determines the increase of defects in structure associated with dangling bonds of carbon atoms and the formation of additional localized states within the band gap. Similar picture is observed for all other Raman spectra of a-C films synthesized at substrate temperature of 50°C and at different argon pressures. Therefore, it can be asserted that the synthesis of amorphous diamond-like carbon films strongly depends on the substrate temperature. Temperature determines the formation of sp^3 coordinated sites in the amorphous carbon matrix.

Significant difference is observed in Raman spectra of a-C films synthesized at the temperature of 250°C and under the pressure of 1.2 Pa (Figure 6). Comparing with spectra shown in Figure 5, G band is shifted towards the high-frequency region by 25 cm^{-1}, also the D band is clearly appeared, i.e. the structure of a-C film becomes a graphite-like one. As it can be seen, the power does not affect the position of G and D bands.



a) 2,5 W/cm^2 b) 2,75 W/cm^2 c) 3,0 W/cm^2

Fig.5. Raman spectra of a-C films synthesized at different values of sputtering power density of plasma discharge, temperature of the substrate T_{sub}=50°C, pressure p=0.5 Pa

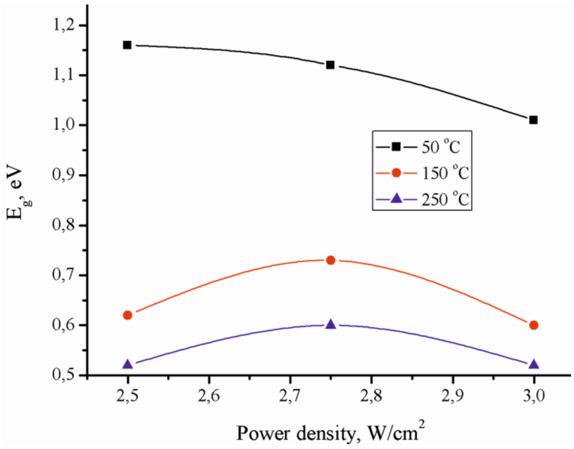


a) 2.5 W/cm^2 b) 2.75 W/cm^2 c) 3.0 W/cm^2

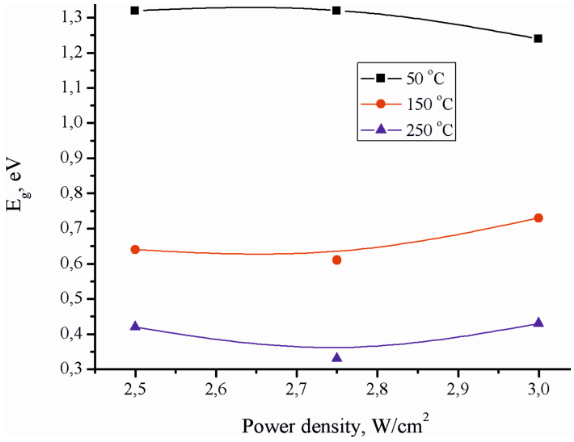
Fig.6. Raman spectra of a-C films synthesized at different values of sputtering power density of plasma discharge, temperature of the substrate T_{sub}=250°C, pressure p=1.2 Pa

To confirm the results of Raman spectroscopy we have conducted study of optical transmission and reflection spectra in the range from 300 nm to 700 nm. The optical band gap of direct-gap transitions for $\alpha \cdot d \sim 1$ was calculated using Tauc method [6], inaccuracy of calculations is ±0.01 eV. Figures 7a and 7b show the Eg as a function of sputtering power of plasma discharge. As it seen, significant changes in optical bang gap at a certain synthesis temperature are not observed.

The changes in Eg do not exceed Δ=0,15 eV. These changes can be associated with insignificant deformation of atomic structure of amorphous carbon lattice, but they are not determined by the ratio of sp^1, sp^2 and sp^3 hybridized bonds. These structural deformations may be caused by the morphology of films' structure.



a) p = 0,5 Pa



b) p = 1,2 Pa

Fig.7. E_g as a function of sputtering power density of plasma discharge at different temperatures and Ar pressures

More distinct changes in the band structure are contributed by the temperature of the substrate. The values of optical band gap of a-C films obtained at the synthesis temperature of 50°C, are greater than 1 eV. According to the paper [7], a-C films with Eg values in the range from 1 eV to 1.8 eV are referred to diamond-like structures. Also, as we can see from Figure 7, as synthesis temperature increases the band gap of films decreases regardless of the argon pressure or sputtering power density. This confirms the results of Raman spectroscopy (Figures 5 and 6). Increase of synthesis temperature leads to the shift of G band to high-frequency region, i.e. the amount of C_6 rings increases. It is related to the increase of sp^2 hybridized bonds, which leads to decrease of band gap.

Conclusion

Comparing the results of atomic force microscopy, Raman spectroscopy and the band gap calculations it can be affirmatively stated that the atomic structure of a-C films synthesized by ion-plasma magnetron sputtering is significantly affected by the temperature of the substrate. Power of plasma discharge in the studied range and the Ar pressure in the working chamber contribute to the formation of the morphology of the film and practically have no effect on the atomic and molecular structure in local and middle atomic order of amorphous carbon film.

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