

STRUCTURE AND PROPERTIES DEPENDENCE OF HYDROGENATED CARBON FILMS ON CONDITIONS OF SYNTHESIS AT Ar+CH₄+H₂ PLASMA

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In this paper we perform study of amorphous hydrogenated a-C:H films, obtained by method of magnetron DC ion-plasma sputtering of high-pure graphite target in Ar+CH₄+H₂ gas mixture. Growth of a-C:H films occurs at sufficiently non-equilibrium conditions, that differ not only by the main thermo dynamical parameters, but also physical-chemical processes of atoms condensation on the substrate. In order to reveal the key parameters, corresponding to the process of self-organization in the chaos of atoms condensation on the substrate, we use atomic force microscopy, Raman spectroscopy and optical spectrophotometry to study surface morphology, local atomic structure and optical properties of a-C:H films, produced at different synthesis conditions (pressure, discharge power and substrate temperature).

Keywords: ion-plasma sputtering, amorphous carbon films, synthesis conditions, Raman spectra microstructure.

Introduction

Amorphous carbon has been widely applied as an anticorrosive coating with good tribological properties in the last decade [1-5]. Thin films of amorphous carbon are chemically stable and have high strength and hardness, therefore they increase the durability of various mechanisms and rubbing parts. In this case it is important to consider carbon films synthesized with hydrogen. The properties of hydrogenated amorphous carbon films (a-C:H) essentially depend on the synthesis methods and conditions [6-10]. It should be noted that the a-C:H films are often synthesized in glow-discharge plasma [8, 10] using hydrocarbon gases as methane, ethylene, acetylene and others.

The method of magnetron DC ion-plasma sputtering of graphite target deserves a special interest. Using this method, it becomes possible to modify the structure of film by various metals [6]. This, in turn, will enhance the possibility to control the properties of amorphous carbon films and their application.

In this work we used the method of magnetron DC ion-plasma sputtering of high-pure graphite target in Ar+CH₄+H₂ gas mixture. The percentage ratio of gas mixture was 92 at.% Ar, 4 at.% CH₄ and 4 at.% H₂. Deposition of a-C:H films was implemented on glass substrates at temperatures of 50, 150 and 250 °C at a rate varied from 20 Å/min to 40 Å/min. The pressure of gas mixture was varied in range from 0.5 Pa to 1.2 Pa for each synthesis temperature. Power density of plasma discharge (w) was 2.5, 2.75 and 3.0 W/cm². We have used cooled magnetron with controlled variable magnetic field. This allowed us to adjust and maintain a certain value of voltage drop and current in the plasma discharge during the synthesis process.

It should be noted that the growth of a-C:H film at 50°C and 150°C is caused by two physicochemical processes: a) sputtering of carbon target by argon ions (PVD) and b) plasma enhanced chemical vapor deposition in vacuum (PECVD) by decomposition of methane molecules. Film growth process at synthesis temperature of 250°C in addition includes the process of thermally activated chemisorption of methane molecules [11]. Thus, the growth of a-C:H film occurs in essentially non-equilibrium conditions, which differ not only by the basic thermodynamic parameters, but also by the physical and chemical processes of condensation of atoms on a substrate. In this case it is impossible to reveal the key parameters, corresponding to the process of

self-organization in the chaos of atoms condensation on the substrate, but we will try to determine how strong the thermodynamic parameters influence on the formation of atomic structure, surface morphology and optical properties of amorphous carbon films.

1. Experimental part

Before synthesis of amorphous carbon film the surface of glass substrates was chemically cleaned by special method using ultrasonic bath and chemical solution based on potassium dichromate, further washed in a solution of ammonia with the following etching in a mixture of hydrochloric acid and hydrogen peroxide, and annealing at 250°C. Final cleaning of the surface includes etching in solution of $\text{HCl} + \text{H}_2\text{O}_2 + \text{H}_2\text{O}$ and holding for 30 minutes in distilled water (18.2 mega ohm resistance) at a temperature of 95°C. After surface cleaning, glass substrates were placed directly into the working chamber with subsequent evacuation.

To study the structure and morphology of a-C:H film atomic force microscope was used (NTegra Therma, Russia). The local atomic structure was analyzed by Raman spectrometer NTegra Spectra (NT-MDT, Russia). Optical transmission (T) and reflectance (R) spectra were investigated using UV-3600 spectrophotometer (Shimadzu, Japan).

Within the structure and surface morphology study "semi-contact" scan mode was applied. It consists of changes of the amplitude and phase of oscillations of cantilever due to the interaction with surface at the level of van der Waals forces of attraction and repulsion. Probes with curvature radius of 10 nm, according to the passport, were used. As one can see from the Figures 1, 2 and 3, the structure of a-C:H films consists of globules with minimum size of about $10 \div 20$ nm. We can observe globules resizing and their conglomeration depending on the synthesis conditions.

2. Results and discussion

Figure 1 shows the surface microstructure of a-C:H films obtained at gas pressures of 0.5 and 1.2 Pa and at constant values of power density $w = 2.5 \text{ W/cm}^2$ and synthesis temperature of 50°C.

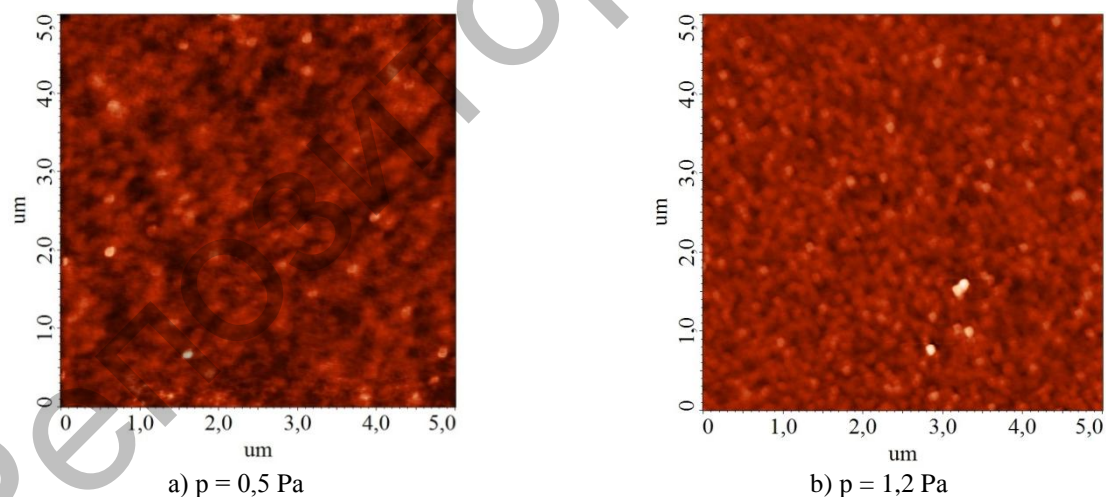


Fig.1. AFM of a-C:H films synthesized at different pressures of gas mixture $\text{Ar} + \text{CH}_4 + \text{H}_2$, constant substrate temperatures $T_{\text{sub}} = 50^\circ\text{C}$ and power density of plasma discharge $w = 2.5 \text{ W/cm}^2$

The fig.1 shows films obtained at the minimum values of plasma discharge power density and substrate temperature. There are also samples synthesized under intermediate gas pressure values. As the Figure shows, the surfaces of films obtained at different pressures of gas are substantially different. At pressure $p = 0.5 \text{ Pa}$ surface morphology has irregularities related to increase globules' size up to 100 nm and conglomeration around the certain attractors. Such formation of surface morphology can be due to the contribution of two unequal processes of condensation of atoms and

molecules to the surface of a-C:H film during the growth: PVD and PECVD. The simultaneous presence of two unequal processes in synthesis of film leads to significant differences between the mobility of condensable atoms and molecules. Mobility of condensed atoms and molecules is determined by their energy. Large energy difference between structural units of carbon on the substrate surface will lead to the formation of large globules and clusters. At the pressure of gas mixture Ar + CH₄ + H₂ p = 1.2 Pa contribution of PECVD in the process of synthesis increases, an energy compensation occurs also due to the increasing number of collisions of carbon atoms and molecules in the gaseous state. It creates certain conditions for the formation of the more uniform film's structure. Therefore in Figure 1b we observe uniformly disturbed globules with size of less than 100 nm.

Influence of substrate temperature on the microstructure and surface morphology of carbon film was studied. Figure 2 shows the changes in microstructure and morphology of a-C:H films at synthesis temperatures of 50°C and 250°C and at constant parameters - power density of ion-plasma discharge 3.0 W/cm² and pressure of gas mixture p=1.2 Pa. As noted above, at the synthesis temperature of 250°C film growth involves three distinct processes that differ by physicochemical parameters. Thermally activated chemisorption significantly differs by energy from PVD and PECVD processes. In [11] was noted that methane exhibits chemisorption properties at temperatures above 200°C. Its adsorption activity increases on the carbon surface. Thus, after the formation of 1 or 2 layers of hydrogenated carbon in the result of PECVD and PVD processes, film growth process additionally includes the process caused by chemisorption of methane molecules activated by temperature of substrate.

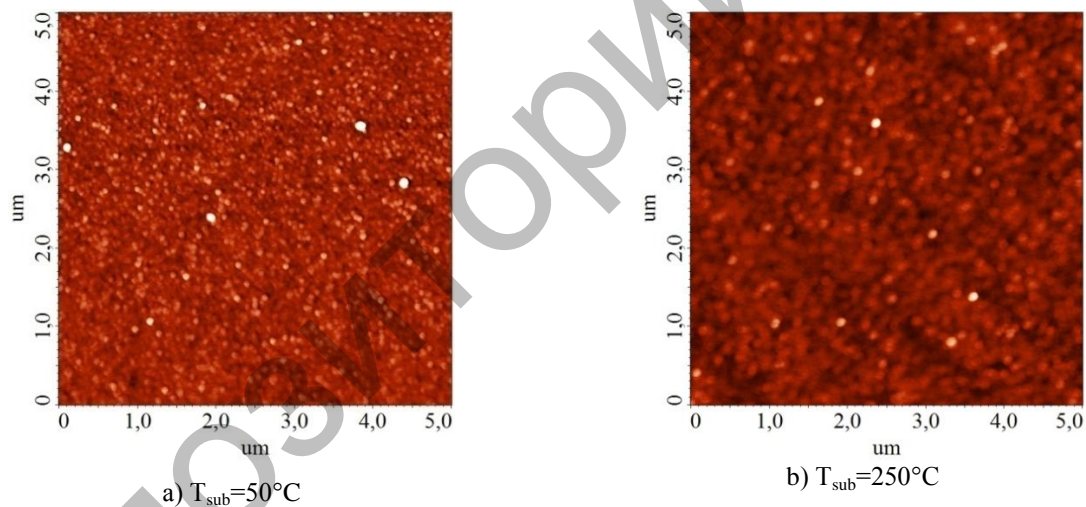


Fig.2. AFM of a-C:H films synthesized at different substrate temperatures, constant pressure p=1.2 of gas mixture Ar + CH₄ + H₂ and the power density of plasma discharge w = 3.0 W/cm²

As figure 2a shows, at a substrate temperature of 50°C, the film structure mainly consists of globules about 10 ÷ 50 nm in size. The morphology of the surface is close to perfectly uniform. Another picture we see in a-C:H film synthesized at a substrate temperature of 250°C (Figure 2b). Globule size has increased up to 100 nm and more. Unequal distribution of globules on the film surface may be explained by the appearance of additional condensation process and five times higher synthesis temperature.

Another important parameter of the synthesis of hydrogenated carbon films is the specific power of discharge. In PECVD processes the structure formation and properties of a-C:H films will depend on the power density or field strength between the electrodes at a constant discharge current [12]. Using a gas mixture Ar + CH₄ + H₂ simultaneously with PVD process the PECVD process

always takes place. We consider the process of film growth at a substrate temperature of 50°C to exclude the influence of thermally activated chemisorption.

Figure 3 shows the AFM scanning of films obtained at three different power density of plasma discharge. From figure 3 it is seen that a-C:H film consists of globules of about 100 nm in size. Increase of power density of ion plasma discharge leads to decrease of globules size down to 10 nm and uniform distribution over the surface.

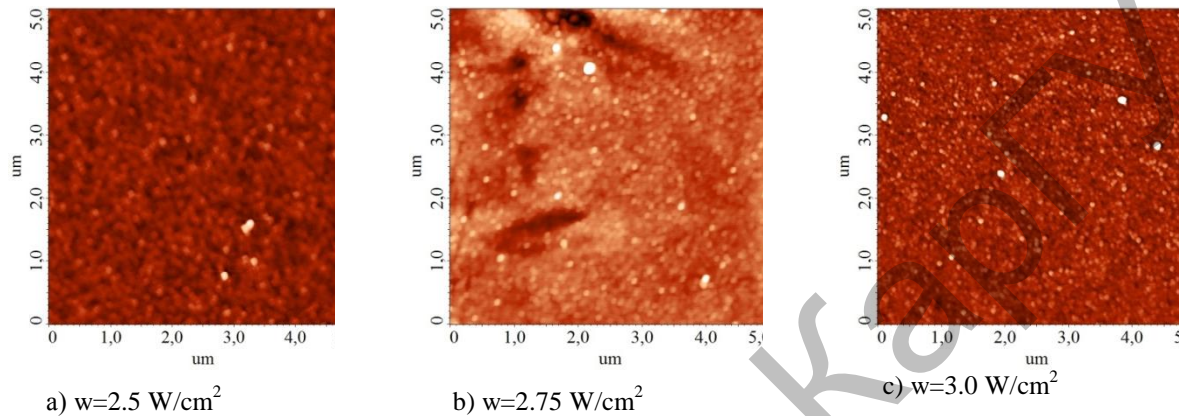


Fig.3. AFM of a-C:H films synthesized at different power density of plasma discharge, constant substrate temperature $T_{\text{sub}}=50^\circ\text{C}$ and pressure $p=1.2$ of gas mixture $\text{Ar} + \text{CH}_4 + \text{H}_2$

To study the local structure of atoms hybridization Raman spectroscopy was used. As the film structure has sufficiently large percentage of carbon atoms bonded with hydrogen atoms, it leads to weakening of carbon matrix hardness and appearance of photostructural transformations under the radiation of 473 nm laser. In order to reduce the effect of laser radiation on the atomic structure of a-C:H film Raman measurements were performed on a moving sample with speed of 5 $\mu\text{m/s}$. The exposure time was 30 seconds, the laser power $\approx 15 \text{ mW}$. Used Raman spectrometer NTegra Spectra enables measurements with an accuracy of $\pm 4 \text{ cm}^{-1}$.

As it is known from [13,14] Raman spectra of carbon films are characterized by two main peaks denoted as D and G. Designation D corresponds to the word "Disordered" and determines the breathing mode of carbon atoms vibrations. Repositioning of D peak is determined in the range from 1350 cm^{-1} to 1400 cm^{-1} depending on the degree of freedom and stiffness of connections between rings and the matrix structure. The Raman spectrum of pyrolytic graphite is characterized by a narrow sharp peak at the frequency of 1581 cm^{-1} and denoted as G, which corresponds to the word "Graphite". The position of G peak is characterized by the translational stretching vibrations of hexagonal rings of graphite structure with sp^2 hybridization. The appearance of defects in graphite structure and additional degrees of freedom in rings consisted of carbon atoms results in breathing mode, i.e. D band.

Figure 4 shows Raman spectra of amorphous hydrogenated carbon films synthesized at plasma discharge power density of 2.5 W/cm^2 and at three different temperatures and pressures of gas mixture $92\text{Ar} + 4\text{CH}_4 + 4\text{H}_2$. The figure shows a significant difference of spectra depending on the thermodynamic parameters of synthesis. Raman spectra are characterized by the main peak, which is denoted as G band and shoulder in the low-frequency region. The appearance of this shoulder is due to the breathing mode of carbon rings. At a substrate temperature of 50°C G peak position is defined at frequency of 1545 cm^{-1} . As it is known [14] position of G band less than 1550 cm^{-1} is characterized by the atomic structure of diamond-like carbon (DLC).

DLC state of structure is characterized by sp^3 hybridized bonds. It should be noted that the increase of working gas pressure as well as the substrate temperature leads to a shift of G band position to that in crystalline graphite. The G band position is characterized by amount of sp^2

hybridized bonds in the amorphous carbon matrix. Approach of G band position to 1581 cm^{-1} may indicate the occurrence of crystalline structural units of graphite in amorphous carbon, the dimensions of which are exceed 1 nm. At a temperature of 250°C we can see clear manifestation of shoulder in the low-frequency region with a pronounced peak at 1360 cm^{-1} . The appearance of D peak is additionally confirmed the formation of rings consisted of carbon atoms and the formation of crystalline clusters. Besides this, it is obvious that with increasing pressure at any temperature the slope of spectra into high frequency region is increased. It is due to the influence of photoluminescence. The appearance of photoluminescence is related to the passivation of carbon free bonds by hydrogen atoms, it reduces density of intra band localized states and reduction of thermalized electrons. Also, as we can see in Fig. 4, that at synthesis temperatures of 50°C and 150°C with increasing gas pressure in the working chamber the intensity of G band decreases. It can be associated with polymerization of structure, which can be connected with increase of double $\text{C}=\text{C}$ and C-H bonds, which leads to the formation of chains and decrease of the amount of clusters consisted of rings.

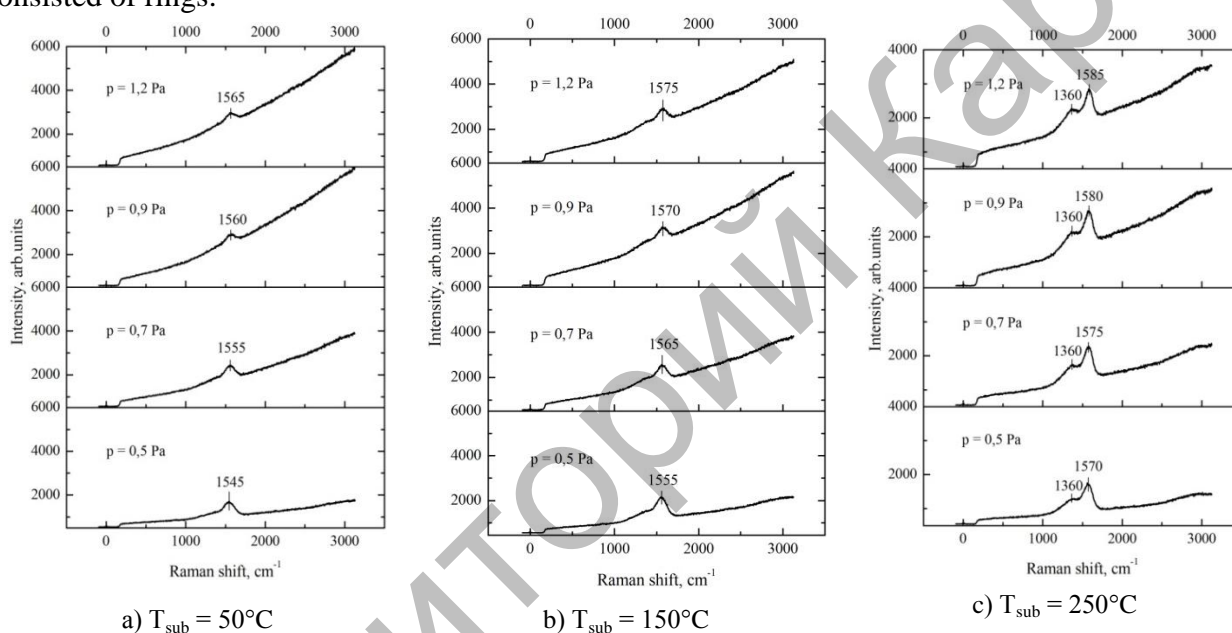


Fig.4. Raman spectra of a-C:H films synthesized at power density of plasma discharge $w = 2.5\text{ W/cm}^2$

It should be noted that trend in changes of the local atomic structure in the range of synthesis parameters being used is similar for all three powers of plasma discharge. Therefore, let's consider the effect of discharge power on the formation of local structure of carbon film in details.

Figure 5 shows Raman spectra for three values of power density of plasma discharge, where it can be seen that the position of G peak is much less than 1550 cm^{-1} and at power of 2.75 W/cm^2 reaches 1535 cm^{-1} . According to [15], the shift of G band towards the low frequency region may increase the sp^3 hybridized bonds and as a result to formation of diamond crystal clusters which can serve as structural attractors.

It can be concluded that in the interval ranging from 2.5 W/cm^2 to 3.0 W/cm^2 at certain thermodynamic parameters of synthesis and mixture of hydrocarbons with argon it is possible to produce diamond-like films with high percentage of sp^3 hybridized bonds. Structurally sensitive parameter that describes properties of matter is the band gap.

We have studied the spectra of transmission and reflection to reveal the regularities and determine the dependence between optical band gap (E_g) and thermodynamic parameters of synthesis. Optical transmission and reflection spectra were measured in the range from 320 to 700 nm.

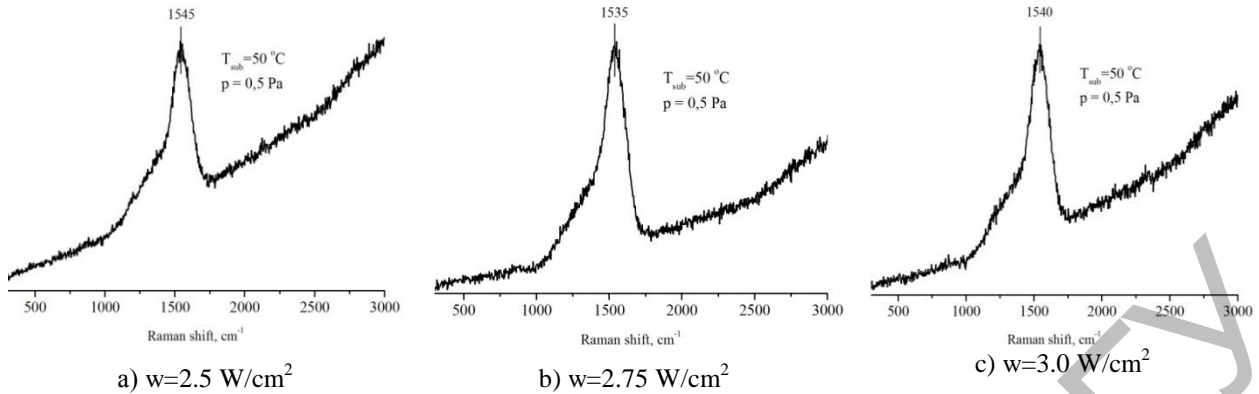


Fig.5. Raman spectra of a-C:H films, synthesized at three different values of specific power of plasma discharge

Figure 6a shows spectra $T(\lambda)$ for two different synthesis temperatures and gas pressures at plasma discharge power density of 2.5 W/cm^2 . Similar picture of transmission depending on temperature and pressure observed for the other two values of plasma discharge power density used in the work. As it seen in Figure 6a increasing the synthesis temperature T_{sub} light transmission in a-C:H films is reduced due to increased number of sp^2 hybridized bonds. At the same time we see that with increasing pressure of the working gas the value of transmittance increases. It may be explained by an increase of the hydrogen concentration in film. The increase of hydrogen results in passivation of carbon dangling bonds. The transmission of light is increased by increasing band gap, which corresponds to decrease of the concentration of unbound electrons. This optical data are in good agreement with the data of Raman spectroscopy, presented in Figure 4.

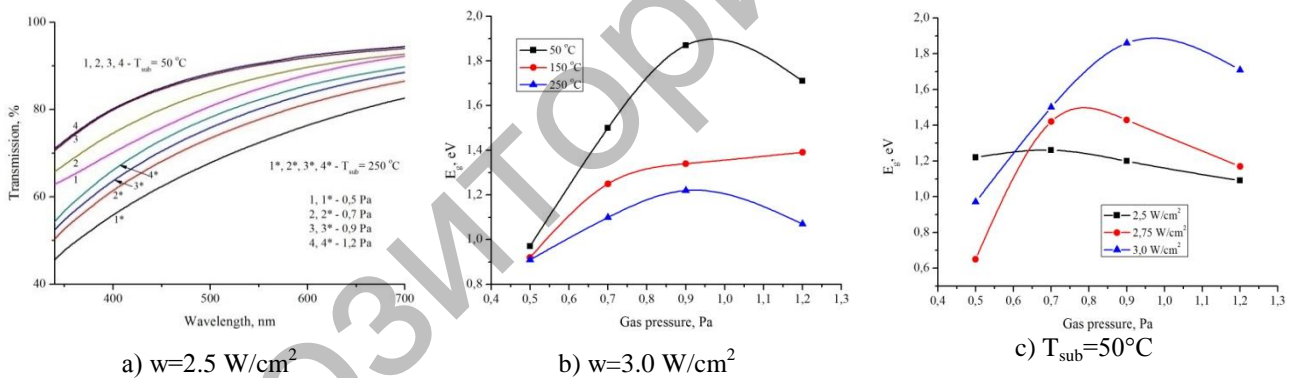


Fig.6. Optical characteristics of a-C:H films synthesized at different thermodynamic parameters

According to the theory of light absorption, developed by Tauc [16], the optical band gap is determined by square law $\sqrt{\alpha h\nu} = B(h\nu - E_g)$, where α – the absorption coefficient, ν - photon frequency. However, in [15] it was noted that in hydrogenated carbon films optical band gap calculated by square law at $\alpha \sim 10^4$ does not correspond to the actual E_g . In [17], the authors proposed an empirical equation for Tauc E_g calculation $E_{04} = 0,46 + 1,06 \cdot E_g$. Therefore, we have calculated the band gap E_{04} using quadratic law of absorption for direct transitions in area $\alpha \sim 10^4$ and then we have defined Tauc E_g using empirical equation.

Figures 6b and 6c show E_g as a function of gas pressure at different temperatures and power densities. The $E_g(p)$ graphs show general regularity: as the gas pressure increases the band gap increases and begins to decrease after reaching the maximum value at $p = 0.9 \text{ Pa}$. Reduction of band gap is associated with increased sp^2 hybridized bonds. In Figure 1, surface microscopy shows that with increasing pressure size of globule decreases and thus, if amount of matter is the same, free surface area increases. The increase of surface results in increasing the unsaturated bonds at carbon

atoms. This unbounded π electrons determine the density of states at the edges of the allowed bands. Lack of hydrogen, as passivator of free electrons, is due to its limited quantity in the gas mixture.

In [15], the authors noted that a-C:H films with a band gap $E_g=1.4$ eV have the highest density of C-C bonds and microhardness, which is due to high content of sp^3 sites in the carbon matrix. Figure 6a shows that a-C:H film synthesized at working gas pressure of 0.7 to 0.9 Pa at 50°C and power density of ion plasma discharge $w=2.75$ W/cm², have band gap $E_g\sim 1.4$ eV, thus, it can be concluded that this is a diamond-like structure with sp^3 content of about 80% or more.

Conclusion

As a result of this work we showed that using a gas mixture of argon, methane and hydrogen, it is possible to control of atomic and molecular structure of the hydrogenated amorphous carbon films over the wide range of synthesis parameters. The reason of such influence of the thermodynamic parameters on the synthesis of a-C:H films is the simultaneous presence of two or three mechanisms involved in the synthesis. And as we found out in this paper, only under certain thermodynamic parameters of DC synthesis it is possible to obtain amorphous diamond-like carbon films with high sp^3 content. It was shown that in a highly non-equilibrium process of condensation of atoms the system organizes itself in a certain way and forms the atomic structure with predetermined properties.

The work was performed as part of grant funding 3219 / GF Committee of Science MES of the Republic of Kazakhstan.

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Article accepted for publication 15.04.2016

Репозиторий КФУ