Amorphous hydrogenated carbon films. Synthesis, structure and properties

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Abstract. Method of high-frequency ion-plasma (RF) sputtering of graphite target in the atmosphere of argon, methane and hydrogen with various ratios was used to synthesize amorphous hydrogenated carbon films (a-C:H) at low power of RF discharge in wide range of temperature and pressure of gas mixture from 0.5 to 0.9 Pa. Structural analysis by methods of atomic force microscopy and Raman spectroscopy showed significant dependence of films structure on thermodynamic and kinetic parameters of synthesis. Change of optical band gap in the range from 1.4 eV to 2.7 eV confirms considerable structural difference of amorphous carbon films obtained at different synthesis conditions. The influence of hydrogen on formation of structure is shown.

1. Introduction

All crystal forms of carbon have very different physical, mechanical and electronic properties. At the same time, the promising material for science and industry is amorphous carbon. Depending on the synthesis methods and conditions, taking a varying degree of hybridization, the carbon atoms in the amorphous phase may form graphite (GLC) and diamond-like (DLC) nanostructures. The amorphous DLC films are widely used as antireflective, chemically inert and durable antifriction coatings for various technical products [1-5].

In the synthesis of thin films, the passivation of carbon dangling bonds by hydrogen atoms takes an important position. Introduction of hydrogen reduces the density of \( \pi \) electrons, which leads to changes of optical, photoelectric and electrical properties.

In the paper it was used radio-frequency (RF) ion-plasma synthesis method using a magnetron at a frequency of 13.56 MHz and a gas mixture of Ar + CH\(_4\) + H\(_2\) in the ratios of 92/4/4 and 84/8/8. Specific power \( (P_d) \) of RF discharge varied from 1 to 1.5 W/cm\(^2\). The average growth rate of the carbon film was \( \approx 3 \) Å / min. Purity of graphite target is 99.999 at.%, the purity of the gases Ar and CH\(_4\) > 99.99at.% The synthesis of films was carried out on quartz substrates.

2. Study of the surface morphology of the a-C: H films synthesized at different thermodynamic and kinetic parameters

The structure and surface morphology of a-C:H films prepared in gas mixture 92Ar + 4CH\(_4\) + 4H\(_2\), were studied by atomic force microscopy (AFM) (NT-MDT, Russia) using contact method with force modulation, which is useful for studying of high-resistance samples with a certain degree of
electrostatic surface potential. In our case the resistivity of a-C:H films was \(10^{14} \div 10^{15}\) (\(\Omega \cdot m\)). Figure 1 shows AFM images of the surface of a-C:H films prepared at 1.25W/cm\(^2\) of RF discharge specific power and at a gas pressure of 0.7 Pa for three different substrate temperatures.

Figure 1. AFM images of a-C:H films synthesized at atmosphere of gas mixture 92Ar+4CH\(_4\)+4H\(_2\) under \(P_d=1.25\) W/cm\(^2\), \(p=0.7\) Pa: a) \(T_{sub} = 50^\circ\) C, b) \(T_{sub} = 150^\circ\) C, c) \(T_{sub} = 250^\circ\) C.

From figure 1 (a) it is seen that the film’s structure consists of tiles of various shapes with sizes of less than 100 nm. The increase of synthesis temperature (fig. 1 b, c) leads to erosion of tile boundaries and at a substrate temperature of 250 °C surface morphology of the film has not any characteristic structural units. Usually the surface of DLC films consists of globules [6]. Therefore, the basis of tiles is not graphite or diamond crystals, but polymer structure, which formation is energetically favorable under the given conditions.

In addition, it was revealed that, the particle size, which determines the structure of the carbon film, increases with increasing gas pressure in the plasma of RF discharge. The increase of specific power leads to the increase of energy of condensing atoms and molecules and therefore to decrease of particles’ size. In addition, there is an increase of the role of carbon and hydrogen ions during the structure formation.

Similar picture is observed for the gas mixture with doubles concentration of methane and hydrogen, i.e. 84Ar+8CH\(_4\)+8H\(_2\). AFM study of the films show, that surface morphology and structure are not uniform. Synthesis conditions significantly affect grain size, i.e. structural unit of carbon film. Depending on the constituent structural units and formation of polymeric chains, structure and form of the grain can be different. AFM data confirm defined in [7] condition of carbon films as nanoheteromorphous structures.

3. Study of the local structure of short-range order in the atomic structure of a-C:H films by Raman spectroscopy (RS)

Study of the local structure by Raman spectroscopy is performed on NTegra Spectra spectrometer (NT-MDT, Russia) with laser excitation of 473 nm (2.62 eV) and power of 1.5 mW.

Let us consider RS of a-C:H films synthesized in atmosphere of gas mixture 92Ar + 4CH\(_4\) + 4H\(_2\) at specific power of RF discharge 1.5 W/cm\(^2\). Figure 2 indicates that at \(T_{sub} = 50^\circ\) C the position of G ~ 1545 cm\(^{-1}\), therefore according to the three-stage model [8], the atomic structure of a-C:H films can be attributed to a diamond-like one, with a percentage of sp\(^3\) hybridized bonds about 70-80%. Due to the increase of sp\(^2\) site, G peak shifts towards the high-frequency region and takes value of 1590 cm\(^{-1}\). At the same time, the appearance of D peak at 1360 cm\(^{-1}\) indicates increasing of C\(_6\) rings.

It was revealed that with increasing specific power of RF discharge, G peak position considerably shifts towards the low frequency region and the amorphous phase of the a-C:H films is partially getting structured, passing from PLC state to the amorphous GLC and DLC structures.
The influence of working gas pressure on the formation of the local structure of a-C:H films was revealed. With increasing pressure of gas mixture 92Ar + 4H$_2$ + 4CH$_4$ we observed the rise of photoluminescence and shift of G peak towards the high-frequency region. Position of G peak is attributed [8-10] to the change of C-C sp$^2$ bonds amount per unit of volume. The increase of the gas pressure increases the number of hydrogen atoms per unit of volume, which in turn increases the formation of C-H bonds. This leads to a reduction of unbounded π electrons and localized states within the band gap. It can be seen from figure 3 that the photoluminescence differs for three different pressures. The rise of gas pressure leads to the increase in photoluminescence. Thus, with increasing pressure the part of sp$^2$ C-C sites increases as well. At the power of 1 W/cm$^2$ and the temperature $T_{\text{sub}}$ = 150°C there is a sufficient concentration of π electrons associated with sp$^2$ C-C and sp$^2$ C-H sites which enough to provide a photoluminescence intensity greater than that of the Raman signal.

At the same time, atomic force microscopy showed that, the increase in pressure leads to the increase in the size of grains forming the structure of the carbon film. Thus, the growth of the grains can be due to the increase in the number of sp$^2$ nanoclusters, which in turn leads to increase of the G peak intensity. Besides, shift of G peak position is due to increase in synthesis temperature.

Comparing the results of Raman spectroscopy with AFM data one can claim that if the structure is formed by particles with sizes of less than 20 nm, then the probability of the formation of nanoclusters with graphite or diamond-like phase is high enough at low specific power of RF discharge. The main criterion for their formation is the synthesis temperature $T_{\text{sub}}$, namely, $T_{\text{sub}} \leq 50^\circ$C is the favorable condition to form DLC nanoparticle, while $T_{\text{sub}} \sim 250^\circ$C and $Pd = 1.5$ W/cm$^2$ promote formation of GLC structures. We have performed additional study about the influence of specific power of RF discharge on the structure of the films. It should be noted that at the specific power ranging from 2 to 3
W/cm\(^2\), \(p = 0.5\) Pa and \(T_{\text{sub}} = 50°C\) the position of G peak is 1545 cm\(^{-1}\), and with the increase of \(P_d\) the trend of Raman spectrum, characterizing the photoluminescence, decreases. This work aims to identify the structural peculiarities of a-C:H films formed at low specific power of RF discharge, and therefore let us focus only on the brief information.

4. The optical properties of the carbon films synthesized by RF method

The bandgap (\(E_g\)) is a structurally sensitive parameter and its value depends on the atomic structure of the film. As it defined in [8], if the band gap of a-C film is less than 1 eV, then the structure of the film is formed mainly of sp\(^2\) bonded structural units and the case of \(E_g = 0\) eV corresponds to the structure of crystalline graphite. The value of \(E_g\) ranging from 1 eV to 2 eV defines an amorphous diamond-like structure formed of sp\(^3\) sites with its content from 40% to 85%.

We performed the study of optical transmission and reflection spectra in the range from 300 nm to 700 nm. As shown in Figure 4, with the increase in the pressure of gas mixture 92Ar + 4CH\(_4\) + 4H\(_2\) in the plasma of RF discharge the \(E_g\) value decreases. Reduction of \(E_g\) in the range from 2.5 eV to 1.45 eV is due to the increase of \(\pi\) electrons.

![Figure 4. Dependence of band gap \(E_g\) on the substrate temperature \(T_{\text{sub}}\) of a-C:H films synthesized at a) \(P_d = 1\) W/cm\(^2\); b) \(P_d = 1.5\) W/cm\(^2\).](attachment:image.png)

Figure 5 shows the plot of \(E_g\) versus synthesis temperature for a-C:H films prepared at different values of pressure 84Ar+8CH\(_4\)+8H\(_2\) and specific power of discharge. \(E_g\) depends on the pressure of the working gas 84Ar + 8CH\(_4\) + 8H\(_2\) and the temperature at \(P_d = 1\) W/cm\(^2\). It can be noticed, that changes in \(E_g\) values correlate with photoluminescence data. Figure 5 (b) shows how much the power of discharge affect the band gap at different pressures and at synthesis temperature of 50°C synthesis. The increase in the gas pressure leads to a decrease in the slope of \(E_g(P_d)\) function. With increasing the gas pressure from 0.5 to 0.9 Pa and the change of \(P_d\) from 1 to 1.5 W/cm\(^2\), the value of \(\Delta E_g\) varies from 1 to 0.5 eV for three temperatures of synthesis. Thus, according to these data, this change of \(E_g\) values can be attributed to the decrease of possibility of carbon atoms to form the various structural units, which determine the atomic structure of the amorphous carbon film.

Comparing the data of Raman spectroscopy and optical band gap, it can be concluded that the G peak position at 1590 cm\(^{-1}\) (fig.2) at the value of the band gap of about 1.5 eV indicates the graphite-like structure, with a small fraction of sp\(^3\) bonds. Hydrogen, as one of the structural elements of the amorphous matrix, incorporates into the structure to form it in such a way that there is a significant change in density of \(\pi\) electrons near the Fermi level. This process widens the band gap in graphite structures.
Figure 5. Dependence of optical band gap on (a) substrate temperature at $P_d = 1 \text{ W/cm}^2$ and (b) specific power of RF discharge at $T_{\text{sub}} = 50^\circ\text{C}$.

Conclusion
The results of atomic force microscopy and band gap values correlate with each other. Thus, the decrease of the grain size, constituting the structure, leads to decrease of $E_g$. The grain size depends strongly on the thermodynamic and kinetic parameters of the synthesis of a-C:H films and this affects the formation of the atomic structure. Changes of the atomic structure are confirmed by Raman spectroscopy data. Using two concentrations of gas mixture of argon, hydrogen and methane it is shown that hydrogen significantly affects the optical properties and structure formation of synthesized a-C:H films.

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