INFLUENCE OF TECHNOLOGICAL PARAMETERS OF PRODUCING a-C:H THIN FILMS ON THEIR STRUCTURE AND ELECTRONIC PROPERTIES

Annotation. Research of working gas composition and film deposition temperature influence on the a-C:H films structure prepared by ion plasma magnetron sputtering, optical and electrical properties was provided. Raman spectroscopy monitored structure of the films. Optimization of technological parameters carried out by the share of sp$^3$-hybridized bonds in the structure of the films and their deposition rate. One can found, that when composition of the working gas was 96% argon and 4% methane and film deposition temperature - 50°C, the proportion of sp$^3$-hybridized bonds is 40% at a deposition rate - 2.5 nm/min. At the same time, these films have a high transmittance in the visible region of the spectrum and electrical conductivity - 5·10$^{-9}$ Ohm$^{-1}$ cm$^{-1}$.

Key words: amorphous carbon films, ion plasma magnetron sputtering, a-C:H thin films

Introduction

Amorphous diamond-like carbon films have a number of unusual properties such as high mechanical strength and transparency in a wide spectral region [1]. Structure of the films represents itself a two-phase system in which the sp$^2$ hybridized carbon atoms situated in the sp$^3$ hybridized carbon matrix [2]. Structure and properties of these films is highly dependent on the technological parameters for their preparation. A-C:H films can be obtained by different methods: selective ion-beam deposition [3], laser-induced physical vapor deposition from the gas phase [4], chemical transport reactions, chemical vapor deposition [5], ion-plasma magnetron sputtering [6]. Among these methods, ion-plasma sputtering method has several advantages - it allows changing wide range of process parameters and modifying films by metal impurities while spraying combined target [7].

The aim of this work was to optimize the technological parameters such as working gas composition and deposition temperature of a-C: H thin films with a diamond-like structure.

Technology preparation, composition and structure control of the films

A-C: H films prepared by ion-plasma DC magnetron sputtering of polycrystalline graphite target with a purity 99.99% at the devices VUP-4 and VUP-5 with an average deposition time - 20 minutes on quartz substrates. Sputtering carried out at the constant positive voltage on the anode. Substrate temperature controlled by copper-constantan thermocouple embedded in the substrate holder. Preparing of the substrates for the films deposition was the following: they placed in K$_2$Cr$_2$O$_7$:H$_2$O:HNO$_3$ solution heated in an ultrasonic bath for 10 minutes and treated with C$_2$H$_5$OH.

Deposition of the films performed with a pressure - 1 Pa, an anode voltage - 600 V and 400 V, and a discharge current - 40 mA. Film thickness ranged from ~ 50 to ~ 100 nm, and determined by scanning of the cleavage a-C:H/a-Si structure using a scanning electron microscope (SEM) Quanta 3D 200i with electrons energies up to 30 keV. (Figure 1)
SEM Quanta 3D 200i also used to control the composition and morphology of the films. Figure 2 and Table 1 show the results of these studies. It has found that impurities are absent in the a-C:H film, in particular, chamber spraying materials and substrate holder materials. This indicates a good localization of ion-plasma discharge on the target. A-C:H films possessed a continuous uniform surface and didn’t contain micro-size defects.

![Energy dispersive spectrum](image1.png)  ![SEM image](image2.png)

**Figure 2.** Energy dispersive spectrum (a) and morphology (b) of the a-C:H thin film

<table>
<thead>
<tr>
<th>Table 1. Composition of a-C:H film according to the results of energy dispersive analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Element</td>
</tr>
<tr>
<td>-------</td>
</tr>
<tr>
<td>C</td>
</tr>
</tbody>
</table>

Note: Wt% - weight fraction, At% - atomic percentages

**Results and discussion**

We studied influence of working gas composition (argon, a mixture of 80% argon and 20% hydrogen, a mixture of 96% argon and 4% methane) and film deposition temperature on their structure. Optimization of technological parameters for producing a-C:H films was to identify the relationship between the composition of the working gas, deposition temperature, and structure of the film, namely the ratio of $sp^3/sp^2$ hybridized bonds.

Raman spectroscopy used to estimate the concentration of $sp^3$ bonds [8]. As is known, there are two peaks in the Raman spectra of amorphous diamond-like films: G peak (graphite-like), which is responsible for the fluctuations of graphite component and located in the area of 1555 cm$^{-1}$, and a peak D (disordered), which is responsible for carbon fluctuations in benzene rings and located in 1400 cm$^{-1}$ [9]. According to the positions of these peaks and the ration of their intensities $I_D/I_G$ one can judge about the structure of the films. Method suggested in [1] used to estimate the proportion of $sp^3$ bonds in the a-C:H matrix. It is the following: firstly it is need to calculate the dispersion of G peak position $(G_1-G_2)/(\lambda_1-\lambda_2)$ in the Raman spectra obtained at different wavelengths of laser excitation. Then, with a usage of dispersion value one can estimate percentage of $sp^3$-hybridized bonds. For diamond-like films, $sp^3$ share should correspond to 40-50%.

Raman spectra obtained at the device Ntegra Spectra using lasers with wavelengths of 473 nm and 633 nm, backscattering power 15 mW. In the figure 3, for example, one can show the Raman spectra of the films deposited at room temperature in working gas mixture - 96% argon and 4% methane, at different wavelengths of laser excitation. The figure shows that with a decrease in a laser excitation energy the ratio of peak intensities $I_D/I_G$ significantly change in the Raman spectra.

There were calculated $G$ peak dispersion of Raman spectra of the films to determine the influence of the working gas composition on the structure including $G$ peak dispersion (see Table 2). Furthermore, during the preparation of the films fixed the influence of the working gas composition on the rate of film deposition.
Table 2. Dispersion of G peak and G peak position of the Raman spectra obtained at the laser excitation wavelength 473 and 633 nm.

<table>
<thead>
<tr>
<th>Composition of the working gas</th>
<th>G peak dispersion: ((G_1-G_2)/(\lambda_1-\lambda_2))</th>
<th>p, Pa</th>
<th>U, V</th>
<th>I, mA</th>
<th>Wavelength (\lambda) of the laser, nm</th>
<th>Deposition rate, nm/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar (96 %)+CH(_4) (4%)</td>
<td>0.22</td>
<td>0.88</td>
<td>600</td>
<td>40</td>
<td>473</td>
<td>2.5</td>
</tr>
<tr>
<td>Ar (96 %)+CH(_4) (4%)</td>
<td>0.26</td>
<td>0.88</td>
<td>600</td>
<td>40</td>
<td>473</td>
<td>1.3</td>
</tr>
<tr>
<td>100% Ar</td>
<td>0.26</td>
<td>0.88</td>
<td>600</td>
<td>40</td>
<td>473</td>
<td>1.3</td>
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<td>0.88</td>
<td>600</td>
<td>40</td>
<td>473</td>
<td>1.3</td>
</tr>
<tr>
<td>Ar(80 %)+H(_2) (20%)</td>
<td>0.21</td>
<td>0.88</td>
<td>600</td>
<td>40</td>
<td>473</td>
<td>1.3</td>
</tr>
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<td>Ar(80 %)+H(_2) (20%)</td>
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<td>473</td>
<td>1.3</td>
</tr>
</tbody>
</table>

Analysis of the results presented in the table showed that films obtained in pure argon, in mixture Ar (80%) + H\(_2\) (20%), Ar (96%) + CH\(_4\) (4%) have a proportion of \(sp^3\) - hybridized bonds equal to (47 ± 3)\%, (38 ± 3)\% and (40 ± 3)\%, respectively. According to [1] from the proportion of \(sp^3\) - hybridized bounds structure of all films is a diamond-like. Importantly, in case of using a mixture of argon with methane, the deposition rate of the amorphous diamond-like film has a maximum value.

The influence of deposition temperature on the Raman spectra of a-C: H films of obtained for the fixed working gas (96%) + CH\(_4\) (4%) showed in Figure 4.
Figure 4. Raman spectra at different deposition temperatures of a-C:H films in the atmosphere (composition of the working gas Ar (96%) + CH$_4$ (4%))

Figure 4 shows that the increase in film deposition temperature leads to a more pronounced manifestation of $D$ peak in the Raman spectra, indicating a greater disordering in film structure. For more detailed identification of changes in the films structure Raman spectra information summarized in the Table 3, which shows the influence of film deposition temperature, when it changes from 50°C to 200°C on the parameters of the Raman spectra.

### Table 3. Influence of temperature on the deposition parameters of Raman spectra of the films.

<table>
<thead>
<tr>
<th>Composition of the working gas</th>
<th>$G$ peak, cm$^{-1}$</th>
<th>$I_D/I_G$</th>
<th>$p$, Pa</th>
<th>U, B</th>
<th>I, mA</th>
<th>$T$, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar (96 %)+CH$_4$ (4%)</td>
<td>1561</td>
<td>0.52</td>
<td>0.88</td>
<td>400</td>
<td>20</td>
<td>200</td>
</tr>
<tr>
<td>Ar (96 %)+CH$_4$ (4%)</td>
<td>1557</td>
<td>0.51</td>
<td>0.88</td>
<td>400</td>
<td>20</td>
<td>150</td>
</tr>
<tr>
<td>Ar (96 %)+CH$_4$ (4%)</td>
<td>1559</td>
<td>0.52</td>
<td>0.88</td>
<td>400</td>
<td>20</td>
<td>100</td>
</tr>
<tr>
<td>Ar (96 %)+CH$_4$ (4%)</td>
<td>1556</td>
<td>0.46</td>
<td>0.88</td>
<td>400</td>
<td>20</td>
<td>50</td>
</tr>
</tbody>
</table>

From Table 3 one can see that with an increase in film deposition temperature $G$ peak in Raman spectra shifts to the low-energy region of the spectrum from 1561 cm$^{-1}$ to 1556 cm$^{-1}$, and varies the ratio of the intensities of $D$ and $G$ peaks. Such changes in Raman spectra show that films’ structure becomes more graphite while the deposition temperature increases.

The optical properties of a-C:H films examined at Shimadzu UV 2000 spectrophotometer on the films with ~ 80 nm thickness. Figure 5 shows the influence of deposition temperature on film transmission spectra for the fixed working gas composition - 96% argon and 4% methane. Figure 5 shows that the maximum transparency observed in the films deposited at 50°C and 100°C temperatures. Increase the film deposition temperature from 100°C to 200°C leads to a slight decrease in transmittance.

Figure 5. Dependence of the films deposition temperature on their transmission.
We note that the change in the composition of the working gas does not affect the optical clarity of films and value of their conductivity.

Conductivity \( \sigma \) films measured on samples with a planar arrangement of electrodes using picoammeter KEITHLEY 6485 with the electric field intensity \( 10^2 \) V/cm in the linear region of current-voltage characteristics. Dependence of conductivity \( \sigma \) of the a-C:H films (\( \sigma \) measured at 300 K) obtained at different deposition temperatures showed in Figure 6.

![Figure 6. Influence of film deposition temperature on their conductivity](image)

The figure shows that minimum conductivity have the films obtained at 50°C. Increase film deposition temperature from 50°C to 200°C results in conductivity increase in 4 orders of magnitude. This indicates that in the structure of a-C:H films noticeably increases the proportion of graphite phase.

Thus, increase the a-C:H film deposition temperature with fixed working gas composition leads to decrease in the optical transmittance and increase in conductivity due to increased \( sp^2 \)- hybridized bonds in their structure.

**Conclusion**

Research of the influence of the working gas composition and a-C:H film deposition temperature on the structure, optical and electrical properties are provided. One can show that change in the working gas composition from argon, mixture of 80% argon and 20% hydrogen to mixture of 96% argon and 4% methane at the fixed film deposition temperature has little influence on the diamond-like films structure. When the working gas composition was 96% argon and 4% methane, there were the highest rate of film deposition -2.5 nm / min. It has found that increase of the film deposition temperature at a fixed gas composition 96% Ar + 4% CH\(_4\) reduces optical transmission and conductivity increase. These changes are associated with the graphitization of the matrix of diamond-like films.

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**BIBLIOGRAPHY**


Физико-математические науки


Михайлова С.Л., Мухаметкаримов Е.С., Дауткхан К., Прихожко О.Ю., Манабаев Н.К., Максимова С.Я., Исмаилова Г.А., Аширова Т.К.

А-С:Н жұқа кабыршактарының электрлік модельдің параметрлерінің олардың құрылымы мен электрлік касиеттерінің сәрі

Түйіндеме. Жұмыстық ғылымдың арқасында а-С:Н-тің аморфтық құрылымы жүргізілді. Құрылым түрлі жақындықтарын зерттеудің маңызы болады. Аморттый құрылымдар құрылымында және олардың түнің құрылымының құрылыс жүргіздігі, құрылыс құрылысына және арқылы қалған киімнің электрлік параметрлерінің құрылысына байланысты. Технологиялық параметрлерді оптимизация құрылымның электрлік касиеттерін көрсетеді.

Резюме. Проведены исследования по влиянию состава рабочего газа и температуры осаждения пленок а-С:Н на их структуру и электрофизические свойства.

Влияние технологических параметров получение тонких пленок а-С:Н на их структуру и электрофизические свойства

Ключевые слова: Аморфные углеродные пленки, ионно-плазменное магнетронное распыление, тонкые пленки а-С:Н

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БЕЙСЫЗЫҚ МАТЕМАТИКАЛЬЫҚ МАЯТНИКТИҢ ТЕРЕБЕЛІСІН МАТНСАЙ КОЛДАНБАЛЫ ПРОГРАММАЛАР ПАКЕТИ КОМЕГІМЕН ЗЕРТТЕУ

Аннотация. Макала бейсызқы математикалық маятниктін тербелісін санылық эдістерді колданып зерттеуге арналған. Сандық эдістер MathCAD колданбалы программалар пакеті комегімен ықшам екірілген. Маятник тербелісінің санның сипаты ашытының 1- ретті толық эллиптичжық интергол қарабағырлыған. 1- ретті толық эллиптичжық интергол ушин санылық қатар сүрөтінде қорытқылы шығарылған. Сандық қатар тербелісінің функціясын ы. = [0; 1; 2; 5; ] мәндегі ушин тербеліс фазасы мәндеріне тәуелділік графигі салынып, өл қалады тақырыланған. Компьютерлік эксперименттер комегімен ықшам екірілген және бейсызқы математиктердін тербелістері салыстырылған.