Electric properties of carbon films deposited by magnetron sputtering with ion assistance

M A Grushin, E A Kral’kina, P A Neklyudova and A M Nikonov

Moscow State University, Moscow, Russian Federation

E-mail: mikhaigrushi@yandex.ru

Abstract The paper deals with the study of ion assistance impact on structure and electrophysical properties of the carbon films deposited by magnetron sputtering of graphite targets. The flow of assisting ions was generated in the plasma reactor based on inductive RF discharge located in the external magnetic field. The change of the ionic current density in the range from 0.5 to 1 mA/cm² was provided. Ion energy was changed by biasing the substrate in the range from 10 to 85 V. Neon, argon and krypton were used as working gases. The electrophysical properties of carbon films are shown to depend non-monotonous on energy of the assisting ions.

1. Introduction

Improving existing and development of new electronic devices require formation of films structures with various predetermined properties. A specific place among film structures is held by carbon films being the most perspective materials of future. This is due to the fact that on the basis of various carbon modifications, it is possible to obtain electronic devices, which properties meet the requirements of almost all units of electronic industry.

Carbon exists in three main allotropic modifications (diamond, graphite, carbide [1]) corresponding to three various hybridization states (sp³, sp², sp¹ respectively). Besides, there are other modifications corresponding to the intermediate hybridization states (fullerenes, nanotubes). It is known that the structure of synthesized films significantly depends on a method of their formation. As a rule, there are carbon atoms possessing all three hybridization states in a volume of a film [2, 3]. As a result the properties of a film depend on a ratio of the components possessing various hybridization states of carbon atoms.

One of the relevant missions of thin film deposition technology is implementation for practical industrial applications environmentally friendly and safe vacuum plasma processes. In this work the dependence of electrophysical properties of carbon film obtained in vacuum by magnetron sputtering on ion assistance parameters was studied. The distinguishing feature of work is using high density fluxes of the assisting ions.

2. Experimental part

Formation of samples was carried out in the hybrid plasma system [4] including a magnetron source equipped by graphite target and a high-density plasma source based on the inductive discharge located in the external magnetic field. The sputtered carbon atoms were deposited on substrates from various materials. Samples were obtained by a combination of magnetron sputtering with simultaneously bombarding by a high-density flow of the accelerated ions.
The range of external parameters of inductive RF discharge with external magnetic field provides the achievement of the resonant excitation of the helicon and TG waves. It allows to optimize a RF power coupling to the discharge and to obtain high-density plasma. Under near resonance conditions it is possible to obtain extended areas of homogeneous plasma. The optimized modes of a plasma system are used for studying influence of the assisting ions flow on structure and properties of carbon films.

For excitation of an inductive RF discharge the solenoidal antenna located on an outer surface of a quartz chamber is used. The antenna ends are connected to RF generator with a working frequency 13.56 MHz and a power output \( P_{\text{gen}} \) up to 1000 W. When a longitudinal magnetic field is imposed on the discharge, an extended plasma column is formed in the process chamber. The diameter of the plasma column is approximately equal to 20 cm. Distinctive feature of the plasma reactor is formation of high density fluxes of the assisting ions, i.e. ion current density is 1 mA/cm\(^2\) at the RF generator \( P_{\text{gen}} = 1000 \) W and 0.5 mA/cm\(^2\) at \( P_{\text{gen}} = 500 \) W. Four series of samples were prepared. They differed by type of the assisting ions and power of RF generator. Argon, neon and a krypton were used as working gases. In Table 1 parameters of each series are represented.

### Table 1. Conditions of experiments.

| Series | \( P_{\text{gen}}, \) W | Current density of assisting ions, mA/cm\(^2\) | Type of assisting ions |
|--------|-----------------|---------------------------------|-----------------|
| 1      | 1000            | 1                               | Ar              |
| 2      | 500             | 0.5                             | Ar              |
| 3      | 1000            | 1                               | Kr              |
| 4      | 1000            | 1                               | Ne              |

In each series of experiments the samples were prepared using different bias voltages \( U_{\text{sh}} \) of a substrate. The bias voltage changed in the range from 0 to – 70 V in respect to the vacuum chamber walls potential. Plasma potential in respect to the chamber walls was about + 15B. Thus, at certain bias voltage energy of the assisting ions was 15 eV higher.

### 3. Results and discussion

For morphology research the samples surface and cross section images in the scanning electron microscope Supra-40 were made. They are represented in Table 2. In the first line images of a cross-section with the characteristic scale of 20 nanometers are represented. In the second and third lines the morphology of the samples surface with the characteristic scales 200 and 20 nanometers are shown correspondingly.

The film grows in all cases perpendicular to a substrate. The film has tubular structure, the diameter of tubes is about 20 nanometers. With assisting ions energy increasing the uniformity of tubes declines in the direction, perpendicular to a substrate. As well the orderliness of a film growth along a surface appears. In the case when \( U_{\text{sh}} = 0 \) V a sample surface is almost uniform, and in the case when \( U_{\text{sh}} > 0 \) (see the second and third column of the Table 2) the existence of strips on a film surface is visible. The length of strips is more than 1 micron.

The dependence of carbon films resistance on bias voltage is shown on Figure 1. The dependence of ratio of films resistance to their thickness on the bias voltage \( U_{\text{sh}} \) is shown on Figure 2.
Table 2. Samples surface and cross-section images in the scanning electron microscope Supra-40 for several samples of first series.

| Sample | Surface Image | Cross-section Image |
|--------|---------------|---------------------|
| 1 sample | ![Image](image1) | ![Image](image2) |
| 4 sample | ![Image](image3) | ![Image](image4) |
| 3 sample | ![Image](image5) | ![Image](image6) |

Figure 1. Dependence of carbon films resistance on the bias voltage $U_{sh}$. Working gas is argon, the ion current density is 1 mA/cm².

Figure 2. The ratio of films resistance to their thickness on the bias voltage $U_{sh}$. Working gas is argon, the ion current density is 1 mA/cm².

The dependence of carbon films resistance on the bias voltage $U_{sh}$ for neon, argon and krypton as working gases is shown on Figure 3. The dependence of carbon films resistance on the bias voltage $U_{sh}$ for two different current densities is shown on Figure 3.
Figure 3. Dependence of carbon films resistance on the bias voltage $U_{sh}$. Neon, argon and krypton are working gases, the ion current density is 1 mA/cm$^2$.

It should be noted that sharp resistance increase at assisting ions energy 45 eV appears under conditions that the bias is 30V for all considered series of experiments (figure 3 c-d). With assisting ions mass increasing (potential of ionization decreasing) the resistance peak becomes higher. With gas discharge source power and assisting ions current density decrease the resonant effect becomes sharper.

For definition of crystalline structure electron diffraction in transmission electron microscope (TEM) was executed. The carbon film was deposited on a single crystal of NaCl, which was dissolved in water before tests. Results of electron diffraction for sample number four of the first series ($U_{sh} = 22$V) are given in figure 5 (a,b).

The existence of two reflexes about an external contour of the main aureole is visible at the diffractogram. The interplanar distance was calculated to be close to 0.47 nm. In general, on a diffractogram one can see indistinct rings and a central aureole that shows high amorphous of the studied film.

Results of diffraction for the second sample of the second series ($P_e$=500 W) $U_{sh} = 30$V are given in figure 6.
Crystal inclusions about 150 nm in size were found in the volume of a carbon film of the sample with maximal resistance. These inclusions presumably have laminate structure (one can see the "exfoliated" edge on crystal grain perimeter). The diffractogram of this inclusion represents almost ideal diffraction pattern from a single crystal. A lattice constant is 0.47 nm that corresponds with value obtained for the sample of the first series. In some directions reflexes of the first and third order are brighter, than reflexes of the second order that can be the result of a chain structure of a single crystal.

At energy 45 eV independently from assisting ions type carbon films with high resistivity were obtained. It is explained by formation of single crystal chained inclusions in volume of a carbon film. Resistance of films grows with increasing mass of the assisting particles (decreasing potential of ionization).

4. Conclusion
In this work the dependence of resistance of carbon film obtained by magnetron sputtering on ion assistance parameters was researched. It is shown, that at assisting ions energy 45 eV sharp increase of films resistance occurs independently on assisting ions type and on ion current density. At the same time with ions mass increasing (potential of ionization decreasing) films resistance at the fixed bias voltage grows. With current density decreasing the resonant effect of resistance growth is expressed more brightly. It is shown that at assisting ions energy 45 eV in a volume of a carbon film single crystal inclusions with the characteristic size of 150 nanometers and a lattice constant of 0.47 nanometers are formed.

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References
[1] Guseva M, Savchenko N and Babaev V The influence of ion irradiation on the structure and properties of amorphous carbon films. 1986 Radiation Effects Lett.; 87: 215 224
[2] Aleksandrov A, Streletsikii O, Khvostov V, Faustov A, Novikov N and Zaitsev A The conductivity of heterostructures based on linear-chain carbon. 2012 Moscow University Physics Bulletin 67, 6, 528–531. DOI:10.3103/S0027134912060021
[3] Khvostov V, Guseva M, Aleksandrov A, Tagachenkov A and Streletsikii O Structural and emission properties of amorphous linear-chain carbon. 2012 Bulletin of the Lebedev Physics Institute 39 2 57–63

Figure 6. The photo of the sample number 2 of the second series in transmission electrons (left), the photo of inclusion in a volume of a film (middle), a diffractogram from inclusion (right).
[4] Aleksandrov A, Vavilin K, Kral’kina E, Neklyudova P, Nikonov A, Pavlov V, Airapetov A, Odinokov V, Pavlov G and Sologub V. Plasma Parameters in the Reactor with Simultaneous Magnetron Discharge and Inductive Radio-Frequency Discharge in the Presence of External Magnetic Field. 2018 *Journal of Communications Technology and Electronics*, 63: 374-380. DOI: 10.22184/1993-8578.2016.70.8.104.108