DEPOSITION OF DIAMOND-LIKE FILMS IN HYDROCARBON PLASMA OF VACUUM ARC AND UNBALANCED DC MAGNETRON

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Amorphous hydrogenated carbon films were deposited in the plasma of low pressure arc discharge with evaporated electrode and in the plasma of unbalanced magnetron sputtering discharge in different gas environment (Ar, CH_4). The films were investigated by the micro-diffraction method using a method of transmission electron microscopy. Influence of the deposition technique and the gas composition to the structure of the deposited films have been investigated.

INTRODUCTION

The technique of planar magnetron sputtering as one of the most advanced modifications of the plasma enhanced chemical vapour deposition (PECVD) method, has been developed some years ago. In order to improve the technological flexibility of the deposition process a standart magnetron can be equiped by the additional magnetic system, which creates a special configuration of the magnetic field lines, with their concentration near the cathode area, so-called regime of unbalanced magnetron [1,2]. The plasma source, based on the idea of unbalanced magnetron with large area cathode has been designed and investigated in our laboratory. The general idea of design of the source is to achieve the high deposition rate of dielectric and conductive films on the various insulating and conducting substrates. In our particular case the purpose was to improve the quality and to increase the deposition rate of the diamond-like thin films from the hydrocarbon low-pressure plasma.

EXPERIMENTAL

The water cooled cathode (diameter 23 cm) of a planar magnetron as a target was surrounded by the permanent magnets. The system induced near the cathode surface a magnetic field with the tangential component of $H = 4 \cdot 10^4$ A/m. The power supply, which is the feading direct current source, provides the voltage between the anode and the cathode from 0 to 1.3 kV. The power supply has been equiped by the protective high-speed system against the current overload. Between the magnetron and the substrate a cylindrical plasma-guide with the water cooled coil has been placed. When this coil was on, the standart magnetron regime has been transformed to so-called unbalanced magnetron regime. Distance between the substrate and the cathode can be changed between 5 and 35 cm.

In our second experimental set up, the carbon films were deposited by means of low-pressure arc discharge with evaporated electrode [3]. Experimental conditions for the carbon films deposition in the case of low-pressure arc discharge with evaporated electrode, and in the case of unbalanced magnetron source are shown in Tables 1 and 2, respectively.

Table 1. Experimental conditions for the carbon films deposition in the arc discharge with evaporated electrode, and the measured bound types. Arc current 40 - 60 A, arc voltage 20 - 40 V.

Trail	Gas	Pressure, 10^{-1} Pa	Deposition time, min	Bound type
D-1	-	0.5	3	$sp^2 + sp^3$
D-2	Ar	3	1	sp^3
D-3	Ar	3	2	sp^3
D-4	Ar	3	4	sp^3
D-5	Ar	3	6	sp^3
D-6	CH_4	3	4	sp^3

Table 2. Experimental conditions for the carbon films deposition in the unbalanced magnetron discharge, and the measured bound types. Pressure in the reaction chamber 1 Pa, distance between cathode and substrate is 20 cm, l is a distance from the plasma beam.

Trail	Gas	Current, A	Voltage, V	l, mm	Bound type
1	Ar	2	1000	0	sp^2
2	Ar	2	1000	30	sp^2
3	92%Ar+8%CH_4	3	900	0	sp^2+sp^3
4	67%Ar+33%CH_4	3.5	950	0	sp^2+sp^3

The structure of the carbon films has been investigated by a technique of transmission electron microscopy. Determination of the optical band gap were performed by means of shortwave boundary of absorbtion spectra with using of an optical spectrometer.

Besides, the capacitivity and the electrical strength of films have been measured. Specimens for the testing were obtained in the form of parallel plate capacitor with the film under investigation as an insulator. One of the plates was polished metal substrate, other was formed by means of vacuum thermal evaporation of chromium and deposition through the mask on a surfaces of the films. Films thickness were known from the transmission electron microscopy. The capacitance was measured by means of admittance bridge.

RESULTS AND DISCUSSION

Data on the films growth rate as function of the current through the magnetic coil (I_c), discharge current (I_d), and discharge voltage (U_d) are shown in Table 3. From Table 3 it can be seen that external magnetic field strongly influences the conditions in the discharge and the films growth rate. Besides, and that is also essential, the external magnetic field allow us increase the cathode-substrate distance without decreasing of the films growth rates.

Table 3. The regimes of carbon sputtering by the unbalanced magnetron discharge.

I_c, A	U_d, kV	I_d, A	Growth rate (μm/min)				
			5 cm	15 cm	20 cm	25 cm	30 cm
0	1.2	1.2	0.03	0	0	0	0
100	1.0	2.2	0.09	0.07	0.06	0.06	0.05
200	0.8	4.0	0.15	0.14	0.13	0.11	0.10

Stable operation of the unbalanced magnetron plasma source is difficult to organize in hydrocarbon atmosphere because of poisoning of the electrodes. Formation of diamond-like films takes place not only on a surface of the substrate, but on the electrodes too. As a consequence after some time the discharge becomes unstable, and in the end it stops to burn. This difficulty has been avoided by a separate injection of the working gas (Ar), and of the reactive (CH_4) gas. It has been possible to realize only in unbalanced magnetron regime, when the cathode-substrate distance was large enough. In the latter case an increase of CH_4 content even up to 33 % from the total gas flow, did not lead to the unstable discharge, and the electrodes remain clean. Addition of the coil leads to the plasma focusing, i.e. plasma density becomes significantly higher. It allows us to increase the deposition rate as much as ten times in comparison with the standart regime.

Micro-diffraction analysis of the films shows, that all deposited films were either amorphous or nanocrystallyne. Broad rings can be observed in all of the micro-diffraction patterns. Procedure for determination of the concrete structure is described in [4]. It was found, that films structure formation strongly depends on the method of deposition and the gas setting. Interplanar distance (d) and interatomic distance (r) for the films, deposited by means of low-pressure arc discharge with evaporated electrode and unbalanced magnetron are shown in Table 4 and Table 5, respectively. The values, which are similar to the crystallyne (diamond) structure are marked with * superscripts, whereas the values, which are similar to the amorphous structure are marked with ** superscripts.

Table 4. Interplanar distances (d) and interatomic distances (r), for the carbon films, deposited in the arc discharge with evaporated electrode.

D-1		D-2		D-5		D-6	
d	r	d	r	d	r	d	r
3.36^{*}	4.13	3.36^{*}	4.13	-	-	-	-
2.02^{*}	2.48^{**}	2.04^{*}	2.51^{**}	2.02^{*}	2.48^{**}	2.04^{*}	2.51^{**}
1.58^{*}	1.94	-	-	-	-	-	-
1.26^{*}	1.55^{**}	1.26^{*}	1.55^{**}	1.26^{*}	1.55^{**}	-	-
1.09^{*}	1.34	1.07^{*}	1.32	1.07^{*}	1.32	1.08^{*}	1.35
-	-	0.90^{*}	1.11	-	-	0.91^{*}	1.12
0.84^{*}	1.03	-	-	-	-	-	-
-	-	0.81^{*}	1.00^{*}	0.81^{*}	1.00	0.80^{*}	0.98

Table 5. Interplanar distances (d) and interatomic distances (r) of the carbon films, deposited in the unbalanced magnetron discharge.

D-1		D-2		D-5		D-6	
d	r	d	r	d	r	d	r
0.336^{*}	0.413	0.336^{*}	0.413	0.336^{*}	0.413	0.336^{*}	0.413
-	-	0.202^{*}	0.248^{**}	0.210	0.258^{**}	0.202^{*}	0.248^{**}
0.187^{*}	0.230	0.180^{*}	0.221	0.187^{*}	0.230	-	-
0.163^{*}	0.200	0.158^{*}	0.194	-	-	0.168^{*}	0.207
0.126^{*}	0.155^{**}	0.126^{*}	0.154^{**}	0.129^{*}	0.159^{**}	0.126^{*}	0.154
0.115^{*}	0.141^{**}	0.112^{*}	0.138	0.115^{*}	0.141^{**}	-	-
0.110^{*}	0.135	-	-	-	-	-	-
0.099^{*}	0.122	0.100^{*}	0.123	-	-	-	-
-	-	0.088^{*}	0.108^{*}	0.089^{*}	0.109	0.088^{*}	0.108
-	-	-	-	-	-	0.081^{*}	0.100

The films, deposited by the trail D-1 (see Table 1), are look like the mixture of graphite and diamond-like nanocrystals. So these films have two bound types (sp^2 and sp^3). The films, which are deposited in atmosphere of argon are mixture of amorphous, nanocrystallyne diamond, and small areas, which have crystalline graphite structure. These films have sp^3 bound type. It is possible, that this fact is connected with the destruction of the weak sp^2 bounds, and as a result in decrease of the films growth rate, and decrease of ions energy. Micro-diffraction patterns of the films, deposited with methane admixture qualitatively differ from the others. These films have largest peaks broadening, and the diamond crystals are very small. The formation of structures occurs only through the creation of sp^3 bounds.

It was found, that the structure of amorphous carbon films has been changed with the thickness variation from 20 to 100 nm. The crystallyne order is improving with increase of the thickness of amorphous layers. Stability of the different carbon films as function of time has been investigated. Structure of the films, which were deposited in methane atmosphere, did not change during the year, while the other films were metastable. Their structure had a tendency of improving of the crystaline order in three months period.

Carbon films, deposited in Ar atmosphere without methane (trail M-1) are nanocrystallyne (see Table 5). Diffraction peaks are typical for the graphite. In these films one can observe the small diamond crystals in graphite matrix. With addition into the reaction chamber of 8 % of methane (trail M-3) the amount of the diamond nanocrystals becomes higher, with that a new amorphous graphite and amorphous diamond phases are appear. It was found, that the crystalline order improves with the increase of methane content. In the films, deposited with admixture of 33 % of CH_4 (trail M-4), the amorphous phase is disappeared and the size of graphite and diamond nanocrystals are decreased. One of the most important properties, which show the viciniity of the deposited films to diamond is the optical band gap. For all films the optical band gap ranges from 2.1 to 2.5 eV. These dates are typical for the diamond-like films obtained by another methods, and known from the literature. Value of capacitivity was 1.88 ± 0.05. Electrical strength was weasured from the breakdown voltage. The value of electrical strength was $(1.2 \pm 0.3) \cdot 10^9$ V/m.

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