Equipment for the deposition of thin films of carbon in the conditions of magnetron sputtering and influences of radiation

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Abstract. This paper presents an experimental method for obtaining a single system thin films allotropes (graphite, carbyne, diamond) forms of carbon. The basic idea of the method consists in photoactivation of adatoms carbon on the surface of the substrate by the radiation source in the range from near IR to near UV. The receipt of the particular allotropic phase of carbon, namely diamond-like or carbyne structure is the result of selection of the deposition parameters: power density and spectral composition of the radiation, substrate temperature, mode of operation of the magnetron. The conducted researches allowed to receive DLC films with the density of the radiation flux on the sample is not less than $1.5 \times 10^{-4}$ W/m$^2$ in the wavelength range of 170-255 nm. In the received film carbon content of sp3-hybridized condition was ~30%. The study of the elemental composition of the obtained films was carried out using x-ray photoelectron spectroscopy (XPS). Diagnostics of the structure was performed by electron energy loss spectroscopy (EELS).

1. Introduction

Methods of coating with plasma methods are widely used in industry. To the main methods plasma deposition of allotropic forms of carbon (DLC, carbyne), are the chemical vapor deposition (CVD) from a hydrogen-containing vapor phase [1], the physical vapor-phase deposition [2] and magnetron sputtering [3]. The method of magnetron sputtering on direct current is a kind of sputtering in a glow discharge with a transversal magnetic field. In this method impact of electrons and ions of high energy on the growing film is minimized. Also dispersion can be carried out in an atmosphere of inert gases, in contrast to methods CVD. In this work we consider an experimental method to obtain a single system of thin films of different allotropes (graphite, carbyne, DLC) forms of carbon, which implements the possibilities of sharing techniques of magnetron sputtering and exposed to a radiation flux from a high-temperature black-body model. The main idea of the method is the photoactivation of carbon adatoms on the substrate surface a source of electromagnetic waves in the range from near IR to near UV.

2. Experiment

To solve the problem, we used a facility with the layout presented in Fig. 1. The vacuum chamber 1, the black-body model construction 10 and junction are the main elements of the facility. In the vacuum chamber are located the working section, the magnetron with the DE-24 graphite target 6, and the dielectric shield 13 [4]. The working section includes substrate 4, the sample holder 3,
thermocouple 5, three-axis translation stage with tilt adjustments 2. This design of the working section allows the substrate to be fixed at the optimum deposition rate of the material. Changing the tilt angle of the sample holder, it is possible to choose the optimum ratio of the radiation flux from a high-temperature black-body model and the angle of incidence of deposited atoms on the substrate. In the chamber the optical control system 12 the provision of a spot from the black-body model on a substrate surface is also installed. The emitter 10 is a hollow cylinder with a thin barrier in the center. Such design of the black-body model makes it possible continuously measure the actual temperature and control the radiation flux, which is carried out by photoactivation. The real temperature of the black-body model is measured by means of the automatic spectral micro pyrometer 11. To connect the black-body model and the vacuum chamber, the junction consisting flexible clamping flange 8, an optical filter holder 9, system of cleaning of the input window of the vacuum chamber 7 is used.

Figure 1. Experimental facility:
(1) working vacuum chamber;  
(2) stage;  
(3) sample holder;  
(4) substrate;  
(5) thermocouple;  
(6) magnetron;  
(7) system of cleaning;  
(8) flexible clamping flange;  
(9) optical filter holder;  
(10) black-body model construction;  
(11) micropyrometer;  
(12) optical control system;  
(13) dielectric shield.

The substrates used in our study were p-Si(100) wafers. Before the experiment, the substrates were cleaned in an alcoholic solution of boric acid, in 98% alcohol and then in distilled water. The purified substrate was annealed at a pressure of ~ 10^{-3} Pa and a temperature of 400°C. The chamber was filled with high-purity argon. After carrying out the experiment substrate was cooled in argon under a pressure of ~100 Pa.

The magnetron power was 70 W, substrate temperature of ~780 K, the temperature of the black-body model from 300 to 3000 K. Used broadband filters, area of transmittance wavelength range which of 255-390 and 510-2700 nm.

3. Results

The film diagnostics included analysis of the elemental composition by X-ray photoelectron spectroscopy (XPS) and structural analysis by electron energy loss spectroscopy (EELS). The investigations were carried out using an electron-ion spectrometer [3].

The energy spectra of electrons emitted under X-ray irradiation indicate the presence of carbon (C) ~93 at.%, oxygen (O) ~5 at.%, and nitrogen (N) ~5 at.% in the film. The electron-energy-loss spectra in the range of characteristic electron-energy loss of the films (\(\pi\) and \(\pi+\sigma\) plasmons) and the spectrum of the DE-24 graphite surface are shown in Fig. 2. For clarity, the spectra are normalized to the elastic peak intensity. The measurements were carried out with a 3 keV probe electron beam. The small shift of the plasmon (\(\pi+\sigma\)) peaks of the samples with respect to DE-24 graphite can be caused by several factors (such as the film structure and the surface geometry). The change in the \(\pi\)-plasmon peak intensity (the area under the peak) indicates a change in the concentration of atoms in the \(sp^3\)-hybridized state. The area under the peak for film 3 decreased by 25–30% with respect to the peak
of sample 1, which indicates a corresponding increase in the number of $sp^3$-hybridized atoms in the sample.

![Graph of energy loss vs. intensity in EELS](image)

**Figure 2.** A fragment of EELS in the region of $\pi$ and $\pi + \sigma$ plasmons.

![Surface image](image)

**Figure 3.** Surface image.

On the surface image Fig. 3, made on an optical electron microscope Phenom with an increase of 12 thousand times, you can see two areas. The upper left region was in a "shadow" with a minimum of the density of the incident flux. On the right, below you can see the intensive growth of crystals under the action of the radiation flux from the black-body model.

4. Discussion

The presence of oxygen and nitrogen can be explained by the high adsorption of the carbon film surface. The low oxygen and nitrogen concentrations indicate that these elements are mainly present in the film surface layer. Thus, we can conclude that the films prepared are of high chemical purity.
The study of the structure of films obtained at different flux density of radiation from a blackbody models showed that sample 3 has a volume content of the number of atoms in sp3-hybridization of valence electron levels of the order of 30%. This film are referred to as DLC films [5]. In the samples obtained with filters, the change in the concentration of atoms in sp3-hybridization of electrons of the valence levels was not revealed. The transfer of the neutral (bivalent) carbon atom with the 1s22s22p2 configuration into the excited (four valent) state with the 1s22s1p3 configuration requires an energy of ≈4.15 eV/atom, which corresponds to the photon wavelength of ~300 nm. The proceeding from the Grotthuss–Draper law, the operating spectral range for the blackbody radiation flux was assumed to be 170–255 nm. Estimates showed that a radiation flux in the spectral range of 170–255 nm is of the order of 1.5·10–4 W/m2.

5. Conclusions
Summing up, we can state that chemically pure DLC can be formed by magnetron sputtering of a graphite target and activation of the deposition surface by a radiation flux.

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