Abstract — Compression erosion plasma flows (CEPF) of a preset composition governed by a material of an inner electrode were first used to obtain nanostructured copper/carbon (Cu–C) thin films. CEPF were generated by a specially designed quasi-stationary erosion plasmodynamic system (QEPS). In such a system, the material of the inner electrode is evaporated and ionized by an electric discharge. Resultant plasma is accelerated and compressed due to the interaction between the discharge current ∼100 kA and azimuthal self-magnetic field. The composition of a compression flow is determined by the material of the inner electrode. The copper-graphite combination electrode was used in the experiment. As a result, copper/carbon thin films ∼1 µm thick were obtained on silicon substrates. Scanning electron microscopy (SEM) and atomic-force microscopy (AFM) images show that the surface of the Cu–C thin films is uniformly covered with nanoscale (25–30 nm) spherical formations. Copper/carbon nanostructured films feature a friction coefficient as low as ∼0.15 and high wear resistance. The mechanisms for the modification of tribological properties of thin-film copper/carbon nanocomposites and the film composition and microstructure are discussed.

1. Introduction

At present the thin-film amorphous metal-carbon (Me/a–C) composites are of apparent scientific interest as some of their physical properties vary over a wide range depending on the metal doping level, the $sp^2/sp^3$ ratio of hybridized carbon bonds, the level of residual mechanical stresses, and the state of surface morphology [1, 2]. In most cases amorphous carbon (a-C) shows such unique properties as an optical transparency in visible and IR regions, chemical and radiation stability, high electrical resistance, low friction coefficient, and high wear resistance. The additional doping of a carbon matrix with metal makes it possible to essentially change the material structural-phase state and thus to modify its strength and tribological properties [3]. Therefore the approach associated with metal doping of carbon coatings is now considered a promising technique to decrease their mechanical stresses and improve adhesion strength and wear resistance without a considerable degradation of the film hardness.

Exposure of different materials to compression erosion plasma flows (CEPF) of the preset composition generated by a quasi-stationary erosion plasma accelerator of a butt-end type [4] opens up fundamentally new possibilities for the formation of composite metal-carbon nanostructured films with unique physical properties. The plasma composition in such an accelerator is determined by the electrical erosion products of a material of the inner electrode through which butt end the discharge currents of ∼100–200 kA are passing. Such a plasmodynamic system (QEPS) effectively operates both in vacuum and in various gases under pressures up to atmospheric one.

With the QEPS inner electrode being made of copper, the compression plasma flow velocity changes in the range $(2–7) \times 10^6$ cm/s depending on experimental conditions.

The present work reports the results of research into mechanical properties and the structure of copper–carbon (Cu–C) thin films with different carbon content that form under the effect of the QEPS-generated compression erosion plasma flow on silicon wafers.

2. Experimental

The experiments were carried out on QEPS whose camera was filled with a buffer gas (air) up to the pressure $P_0 = 100$ Pa. The QEPS inner electrode was made of copper with a graphite rod pressed-in. As a consequence, the discharge of the accelerator produces the compression erosion plasma flow that contains atoms and ions of both copper and carbon. The action of such a plasma flow on the silicon wafer results in the melting of a thin surface layer and a subsequent synthesis of a copper-carbon film ∼1 µm in thickness.

Exposed to plasma flows were the (111) mono-crystalline silicon wafers measuring $10 \times 10 \times 0.28$ mm.

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The energy density transmitted by the compression plasma flow to the sample surface varied from 2.5 to 4.5 J/cm² depending on the initial voltage of accelerator energy storage and the distance from the butt end of discharge device to the sample. Such a range of energy densities at the exposure duration of ~100 µs corresponds to variations of power density \( P \) from \( 2.5 \cdot 10^4 \) to \( 4.5 \cdot 10^4 \) W/cm².

To study the structure and mechanical properties of the obtained copper-carbon thin films, Raman spectroscopy, scanning electron microscopy (SEM), were used along with tribological and indentation tests. The elemental composition of copper-carbon films obtained using CEPF was analyzed by means of Auger electron spectroscopy (AES) with a Perkin Elmer PHI-660 Auger spectrometer.

Morphology of the films’ surface was studied with the help of a Leo 1455VP scanning electron microscope (SEM). Samples were tested for microhardness with PMT-3 instrument under the load of 0.5 N. Ten measurements were carried out for each load value after which the results were averaged. Relative accuracy of hardness measurements was ~5%. The surface topography of film was determined using a scanning probe microscope “Solver P47-PRO” in tapping mode.

The tribological tests were of “pin-on-plane” type, dry sliding dynamic friction. The linear velocity was 2 mm/s. The pin was made of a hard alloy (92 wt.% WC, 8 wt.% Co). The normal load on the pin was 0.1 N.

The values of concentration of carbon and copper in films obtained at different power densities transmitted by the compression plasma flow to the sample surface are shown in the Table.

The values of carbon content of films deposited under different power densities \( P \), and also the results of mathematical treatment of Raman spectra for Cu–C films with different carbon content

<table>
<thead>
<tr>
<th>( P \cdot 10^4 ), W/cm²</th>
<th>Carbon concentration, at.%</th>
<th>( D_{\text{peak}} ), cm⁻¹</th>
<th>( G_{\text{peak}} ), cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>90</td>
<td>1333</td>
<td>1600</td>
</tr>
<tr>
<td>3.0</td>
<td>95</td>
<td>1368</td>
<td>1580</td>
</tr>
<tr>
<td>4.0</td>
<td>88</td>
<td>1346</td>
<td>1590</td>
</tr>
</tbody>
</table>

3. Results and discussion

The surface SEM images of copper-carbon films produced using compression erosion plasma flows at different energy densities show the changes both in the surface morphology and in the microstructure of samples (Fig. 1). The film surface obtained at power density of \( 2.5 \cdot 10^4 \) W/cm² and containing 90 at.% of carbon is sufficiently smooth (Fig. 1, a) but large formations ~700 nm in size are present in the film. At the same time the SEM image taken using reflected electrons makes it possible to conclude that these surface formations are mainly from copper. As for the films forming at \( 3.0 \cdot 10^4 \) W/cm² power density and containing 95 at.% of carbon, their surface consists of the formations evenly size-distributed (Fig. 1, b).

\[ P = 2.5 \cdot 10^4 \text{ W/cm}^2 \]  
\[ P = 3.0 \cdot 10^4 \text{ W/cm}^2 \]  
\[ P = 4.0 \cdot 10^4 \text{ W/cm}^2 \]  
\[ P = 4.5 \cdot 10^4 \text{ W/cm}^2 \]  

Fig. 1. The surface images of copper-carbon films produced using compression erosion plasma flows at different power densities, performed by scanning electron microscopy (SEM)

The increase of power density up to \( 4 \cdot 10^4 \) W/cm² results in the appearance of larger formations on the surface of film with carbon concentration of 88 at.%. Thus the size of such formations varies from 50 to 500 nm (Fig. 1, c). The subsequent growth of power density up to \( 4.5 \cdot 10^4 \) W/cm² results in the generation of large and small globular formations (Fig. 1, d) on the surface of the film with carbon content of 85 at.%. The size of the formations ranges from 100 nm up to 1 µm. In addition, the SEM images obtained using reflected electrons indicate that these surface formations are mainly from copper.

The analysis of the results obtained shows that the microstructure of synthesized copper-carbon films considerably depends on power density, \( P \), transmitted by the compression plasma flow to the sample. The small spherical formations ~25–30 nm in size dominate at relatively low values of power density.

The increase of \( P \) results in the formation of small (~100 nm) and large (up to 1 µm) copper crystallites introduced in the carbon matrix which is associated with the features of the erosion process of the compositional electrode that manifest themselves with the increase of the energy contributed to the QEPS discharge.

In view of the facts that copper and carbon do not form carbides and the carbon concentration in these films is very high (85–95 at.%), it was of interest to trace the dynamics of the carbon state change with the growth of power density in plasma. Raman spectroscopy is the most suitable method to do this.

Raman spectra for Cu–C films of various carbon contents produced at different power densities are presented in Fig. 2.

The deconvolution of Raman spectra was carried out using Gaussian functions and a linear background
(see the Table). As follows from the analysis of Raman spectra, the variation of the CEPF power density from $3.0 \cdot 10^4$ to $2.5 \cdot 10^4 \text{ W/cm}^2$ and the reduction of carbon concentration from 95 to 90 at.% both result in the shift of the $D_{\text{peak}}$ position towards the low-frequency region to the value of 1333 cm$^{-1}$. At the same time the $G_{\text{peak}}$ shifts towards the high-frequency region to 1600 cm$^{-1}$, and the $I(D)/I(G)$ ratio increases. Such a change in the form of Raman spectra is known to testify the increase in a fraction of nanocrystalline graphite in films with carbon content of 90 at.% [5].

The oscillations of hexatomic rings with the extension and compression of $sp^2$-bonds are known to be responsible for the $G$ line corresponding to 1581 cm$^{-1}$ in the graphite spectrum. In nanocrystalline graphite, the line $G$ shifts towards high frequencies up to 1600 cm$^{-1}$ owing to the dimensional quantization of phonons in nanocrystals. The increase in the $I(D)/I(G)$ intensity ratio and low-frequency shift of $D_{\text{peak}}$ may indicate the association of disordered carbon clusters into larger ordered ones which is accompanied with the decrease in the number of dangling carbon bonds. In such a way, with the decrease in power density to $2.5 \cdot 10^4 \text{ W/cm}^2$ the size of carbon clusters in Cu–C nanocomposites with carbon content of 90 at.% increases, carbon clusters become internally ordered, and the fraction of nanocrystalline graphite grows [6].

The hardness of copper-carbon composites (the Table) produced using compression erosion plasma flows at different $P$ values varies as a function of the structure as Raman spectroscopy shows (Fig. 2).

The copper-carbon film deposited at $P = 3.0 \cdot 10^4 \text{ W/cm}^2$ with 95 at.% carbon concentration exhibited the largest hardness of $\sim 14.5 \text{ GPa}$. According to Raman spectroscopy analysis, the structure of these films comprises small disordered graphite rings, and small formations $\sim 25–30 \text{ nm}$ in size dominate on their surface, which is confirmed by SEM and AFM images (Figs. 1, c and 2).

With the increase of power density up to $4.5 \cdot 10^4 \text{ W/cm}^2$ the hardness of Cu–C composites decreases from 8.0 to $6.5 \text{ GPa}$ (see the Table), which is accompanied by the association of disordered rings into larger clusters, the internal ordering of carbon, and the appearance of larger formations measuring up to 1 $\mu$m (Fig. 1, d) on the surface of films.

The results of friction tests of the composite Cu–C films formed on silicon substrates using compression erosion plasma flows at different power densities are shown in Fig. 3.

The friction coefficient of Cu–C composites with carbon concentration of 90 at.% at $P = 2.5 \cdot 10^4 \text{ W/cm}^2$ is practically constant and equal to 0.23 up to the slip distance of 1.2 m (Fig. 3). Over the length of the slip distance the indenter was gliding over the film surface smoothening its small roughnesses, after which it practically immediately penetrated into silicon.

With the increase in power density to $3.0 \cdot 10^4 \text{ W/cm}^2$ the copper-carbon composite with carbon concentration of 95 at.% is formed. Such film features as low value of initial friction coefficient ($\sim 0.15$), a high hardness ($\sim 14.5 \text{ GPa}$), and as a consequence a high wear resistance, which is confirmed by the fact that the indenter failed to cut the film through even after passing a slip distance of 20 m (Fig. 3).

Copper-carbon films with carbon concentration 88 at.% produced at $P = 4.0 \cdot 10^4 \text{ W/cm}^2$ failed immediately after the indenter penetration into the composite material. These films, while possessing a sufficiently high value of hardness ($\sim 8.0 \text{ GPa}$), seem to exhibit a rather high level of compressive mechanical stresses resulting in such a quick film destruction (see Fig. 3).

The friction coefficient of copper-carbon composites with carbon concentration of 85 at.% produced at $4.5 \cdot 10^4 \text{ W/cm}^2$ power density increases linearly with the increase in the slip distance from 0 to 1.5 m (see Fig. 3). As can be seen from [7], the inclination angle and path length of linear section in the friction coefficient dependence curve are determined by the value of the film volumetric wear per time or the film wear resistance. It is worth to note that the radius of curvature of the indenter ($\sim 1 \text{ mm}$) is a lot more of the film thickness ($\sim 1 \mu$m); hence the friction coefficient will
vary linearly with the slip distance until the indenter reaches a silicon layer.

Though the films with carbon concentration 85 at.% have the least hardness (~6.5 GPa), the wear resistance of these composites is sufficiently high. The cause of the increase in the wear resistance is supposed to be the growth of volume fraction of a graphite film with the low shear stress at the triboccontact between the composite film and the indenter. Such a mechanism for the decrease in the shear stresses during friction was observed for a-C:H films [8].

4. Conclusions

The research on the copper-carbon composites produced using compression erosion plasma flows at power densities in the range of \(2.5 \times 10^4 \text{ W/cm}^2\) enabled a number of main peculiarities of the changes in the structure and mechanical properties of materials under study to be revealed. The research of microstructure by scanning electron microscopy showed that the surface of Cu–C films with 95 at.% carbon content produced at power density of \(3.0 \times 10^4 \text{ W/cm}^2\) consists of the formations with uniform size distribution, the dominant diameter being 25–30 nm. The further growth of power density up to \(4.5 \times 10^4 \text{ W/cm}^2\) results in the copper-carbon film containing 85 at.% of carbon whose surface consists mainly of globular formations varying in size from 100 nm to 1 µm. According to Raman spectroscopy data, with the decrease in the power density to \(2.5 \times 10^4 \text{ W/cm}^2\) the size of carbon clusters in Cu–C nanocomposites containing 90 at.% of carbon increases, the carbon internal ordering occurs, and the fraction of nanocrystalline graphite grows. As for mechanical properties, the copper-carbon composites with carbon content of 95 at.% produced at power density of \(3.0 \times 10^4 \text{ W/cm}^2\) possess the lowest value of the initial friction coefficient (~0.15), the highest hardness (~14.5 GPa), and as a result the highest wear resistance that is confirmed by the longest slip distance of 20 m passed by the indenter in such a film.

References