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The influence of conditions of formation of films of the W-C system during magnetron sputtering of tungsten with the introduction of volatile hydrocarbons into the plasma discharge region

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This paper presents experimental studies on the formation of a WC compound during magnetron sputtering of tungsten in a hydrocarbon environment on the surface of a glass substrate. It has been established that different magnetron operating modes affect the formation and surface structure of the growing film. In the range of voltages applied to the tungsten target, all hydrocarbons used in the experiment completely dissociate in the discharge plasma. Free carbon dissolves in the growing tungsten film, and at relatively low magnetron voltages, two chemical compounds are mainly formed in the W-C system: α -WC and W_2C , with WC predominating. As the magnetron voltage increases, the sputtering rate increases, and the proportion of W_2C increases. In this paper, changes in the surface microstructure of WC and W_2C films are assessed using atomic force microscopy (AFM). The potential of this method for producing compounds of refractory metals with carbon is demonstrated.

Keywords: magnetron sputtering, tungsten, graphite, surface modification, plasma-chemical synthesis.

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Introduction

Carbides of refractory metals have long found wide application in modern technology. One of the most important materials of this series is tungsten carbide, WC. At present, with the development of technologies, the field of application of tungsten carbide is constantly expanding. Modern achievements in materials science make it possible to modify the properties of WC and W_2C by adding, when necessary, various alloying additives to their composition. Such additives make it possible to obtain new properties of well-studied tungsten compounds – such as increased heat resistance or corrosion resistance. Such modifications find application in a wide variety of industries, including medical instruments, aviation and space technology.

Tungsten carbide in its pure form or in a mixture with W_2C and with additions of nickel or cobalt makes it possible to ensure maximum durability of surfaces coated with such materials. Along with this, tungsten carbide is actively used in electronics, where its conductive properties and heat resistance are employed. Such compounds are used in various electronic components as substrates for creating semiconductor devices. In cryogenic technology, tungsten and tungsten-carbon thermoelectric elements are used as sensitive elements for ultrasensitive thermometers.

Every year, research and development in this field become increasingly relevant. Various synthesis methods are used for depositing the above-listed coatings. Vacuum processes – such as a combination of pulsed laser ablation and

magnetron sputtering [1], a combination of reactive RF magnetron sputtering with ion implantation from a plasma source [2], sputtering using a magnetron arc source [3], or co-sputtering of WC and C targets in an argon (Ar) atmosphere [4]. Among these methods, of particular interest is the hybrid technology PECVD (plasma-enhanced chemical vapor deposition), PVD (physical vapor deposition), including simultaneous sputtering of a tungsten target in a reactive hydrocarbon atmosphere – such as C_2H_2 [3, 5], CH_4 [6], or C_6H_6 [7, 8]. Undoubtedly, of particular interest is the dissociation of organic molecules in plasma, leading to the incorporation of WC nanoparticles into a hydrogenated carbon matrix WC/C:H. These results, in combination with atomic force microscopy, make it possible to describe the surface of the deposited film as an aggregate of W_xC_{1-y} crystallites corresponding to an aggregate of small nanograins of W_2C and WC_{1-x} diluted in the hydrogenated carbon matrix. At the same time, the ratio between the hard crystallized WC phase and the softer hydrogenated carbon matrix decreases with increasing hydrocarbon flow. In the present work, the authors obtained tungsten carbide films by magnetron sputtering of a pure tungsten target in a medium of hydrocarbons and the working gas argon Ar at room temperature under various magnetron operating regimes. The authors applied similar methods for obtaining various compounds of the metal with carbon. In previous works [9–13], for example, composite targets of copper and solid graphite were used. However, the sputtering coefficients of copper (2.4 in argon) and graphite (0.12 in argon) at Ar^+ ion energies of 500 eV differ greatly, so it is very difficult to select a suitable regime for the magnetron operation. When sputtering a tungsten target, this difference is noticeably smaller (0.6 in argon), but the process of WC film growth is still poorly controllable. For this reason, a method was chosen of introducing a mixture of readily evaporating hydrocarbons into the region of the plasma discharge. In this region, as is known from the literature, plasma-chemical pyrolysis should occur, that is, the process of decomposition of organic compounds carried out in a low-temperature plasma with average molecular energies on the order of 0.1–50 eV [14–18]. The growth of WC films in our case proceeded at low substrate temperatures (~ 100 °C).

The mobility of the atoms of the deposited substance at such temperatures is low, and crystal growth is inhibited. The resulting fine-crystalline structure was observed by us using an atomic force microscope (AFM).

Experiment procedure

WC coatings were formed on glass substrates by means of reactive magnetron sputtering of a tungsten target in an Ar + C + H plasma. Nefras of grade BR-1 was used as the carbon source. Nefras is a mixture of paraffinic and naphthenic hydrocarbons.

In the experiments, a tungsten plate with a content of 99.93 wt. % of the main element, with a diameter of 70 mm and a thickness of 2 mm, was used as the target. A constant voltage from –600 V to –1400 V, depending on the experiment, was applied to the magnetron. In magnetron sputtering, argon was used as the plasma-forming gas. The experiments were carried out at a constant pressure of argon and the carbon-containing component in a ratio of 1:1. Each gas was supplied through a separate leak valve, after which the gases were mixed and entered the plasma zone in the form of a mixture. The pressure of the gas mixture in the vacuum chamber was maintained at a constant level and amounted to $\sim 10^{-3}$ Torr. Thus, the process of reactive deposition of atoms on the substrate surface was realized. As a result, in the medium of the reactive gas in the plasma, the required compound is formed on the substrate surface. The sputtering rate of the target depended on the voltage applied to it. In the experiment, at the first stage, at three different voltages (560 V, 900 V, 1400 V), a pure tungsten target was sputtered. Thus, at a voltage of 560–600 V, the deposition rate was ~ 1 nm/s, and at a voltage of 880–900 V – ~ 2.6 – 2.7 nm/s; at 1400 V, the deposition rate was 10–12 nm/s [19–21]. For the process of reactive deposition in a medium of argon and carbon at the same voltages, the deposition rates change. In the region of low voltages at the magnetron, the growth of the WC film occurs both on the substrate surface and on the surface of the tungsten target. Therefore, at low voltages the sputtering rates of the target are lower, since sputtering occurs from the already formed WC phase on the surface of the W target,

where the rates of formation of the WC phase and the rates of its sputtering compete [22–24]. Such a state is observed partially also for the average values of the applied voltage.

Only at a voltage of 1400 V is the growth rate of the WC film comparable to the growth rate of the W film. The structural and electrophysical parameters of films deposited under conventional deposition regimes are, in the general case, analogous to the structures of bulk samples. A characteristic feature of WC films is the presence of a minimum of electrical resistivity

in films of stoichiometric composition. It corresponds, for tungsten, to $0.56 \mu\Omega\cdot\text{cm}$ and, for tungsten carbide, to $0.19 \mu\Omega\cdot\text{cm}$, under the condition of good pumping of the vacuum chamber to residual pressure values of $\sim 5 \times 10^{-6}$ Torr, and further reduction of the oxidizing components of the residual atmosphere – by degassing. The surface morphology of the films was studied by the method of atomic force microscopy. Figure 1 presents AFM images of the surface of a tungsten film at different deposition rates.

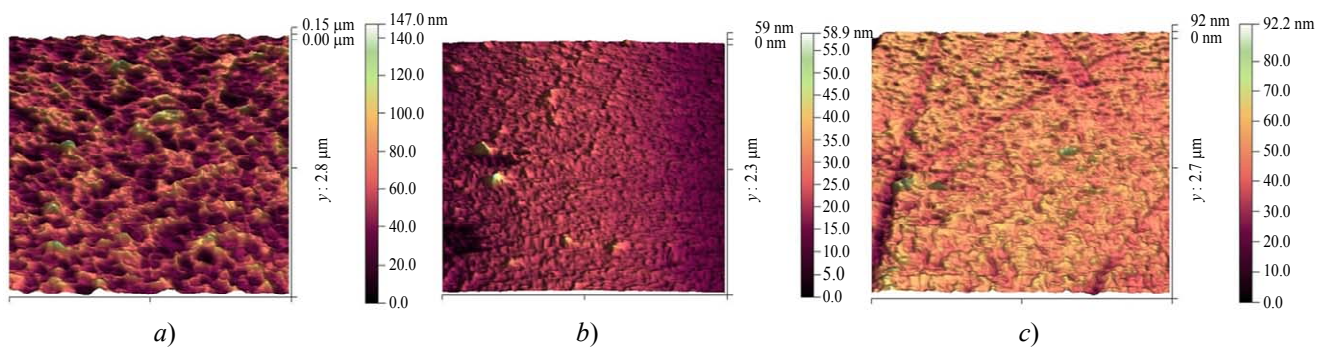


Fig. 1. AFM image of the film surface during sputtering of a tungsten target at different deposition rates. Voltage at the W target: a) – 600 V; b) – 900 V; c) – 1400 V

The images show that with an increasing deposition rate the tungsten surface becomes more uniform. The film surfaces are dense, without large particles, voids, or delaminations, which indicates good adhesion, even though the compressive stress in the tungsten film increases with thickness. At high deposition rates, microcracks appear on the film surface, and at thicknesses of $\sim 1 \mu\text{m}$ and above, the content of other phases increases, which leads to an increase in mechanical stresses due to the mismatch of the parameters of the unit cells of the different phases.

An increase in mechanical stresses leads to an increase in the electrical resistivity of tungsten films and exceeds the resistance of the bulk material by more than an order of magnitude. The films formed on the obtained samples are more uniform and contain mainly the α -phase – this leads to a decrease in electrical resistivity. Figure 2 shows surfaces where tungsten carbide films are

formed. According to literature data [1–5], the formation of WC occurs on the tungsten surface during film growth. Carbon atoms adsorbed on the surface and not having reacted with tungsten diffuse inward, resulting in the formation of W_2C crystals. With an increasing deposition rate and, as a consequence, local heating of the sample surface, the diffusion of C into W is accelerated, the WC content decreases, and W_2C becomes the dominant carbide compound. At low deposition rates, a more ordered but rougher surface is formed. With an increasing deposition rate, the roughness noticeably decreases – this probably occurs due to the lack of time for the formation of larger WC crystals.

It is assumed that under these deposition regimes the content of the pure α -phase of tungsten on the surface and inside the film is minimal, and the metallic tungsten in the near-surface region has completely reacted with carbon, which is confirmed by literature data [6–8].

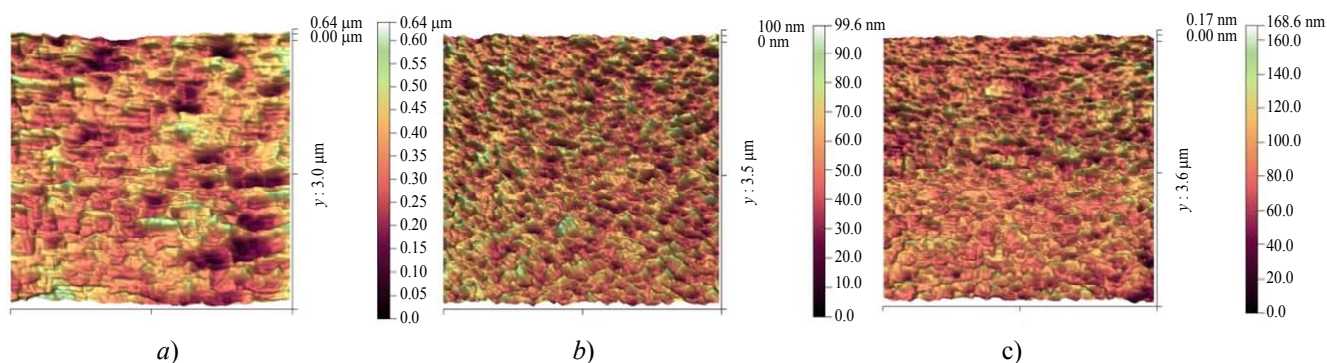


Fig. 2. AFM image of the film surface during sputtering of a tungsten target in a medium of hydrocarbons at different deposition rates. Voltage at the W target: a) – 600 V; b) – 900 V; c) – 1400 V

Findings and Discussion

The study of the film structure was carried out using a Solver P47-PRO scanning probe microscope from NT-MDT. Using atomic force microscopy, the surface morphology of tungsten-graphite films of the composition WC and W_2C was studied in the absence of hydrocarbons during their production. On the basis of the atomic force microscopy data and the particle size distribution plots, an assessment was made of the

characteristic features of the surface relief of WC and W_2C depending on the deposition rate according to key statistical parameters – such as average roughness, root-mean-square roughness, peak-to-valley height, and asymmetry. The results of these studies show a clear difference in the surface characteristics between W and WC films.

In Fig. 3, a plot of the height distribution on the tungsten surface is presented, that is, the dependence of the number of crystallites on their sizes per unit surface area.

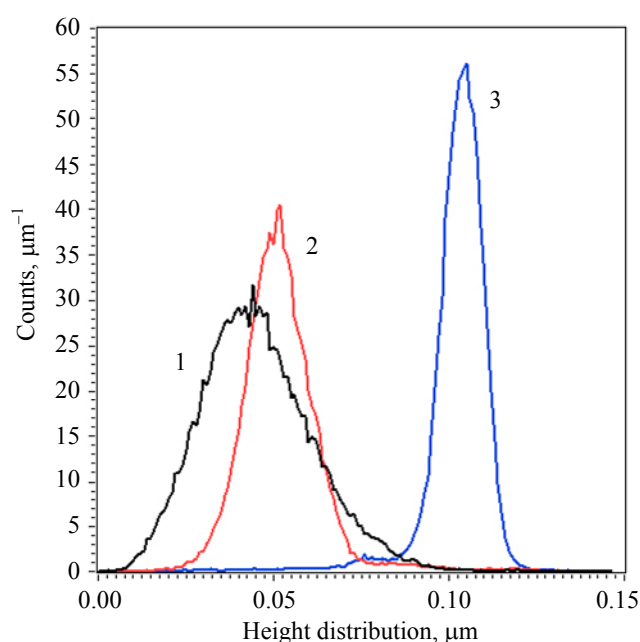


Fig. 3. Height distribution of crystallites on the surface of tungsten films at three deposition rates: 1 – low; 2 – medium; 3 – high

The W films after deposition had a relatively smooth and uniform surface with height variations from 40 to 120 nm. In the presented plot, the width of peak 1 indicates a somewhat greater surface roughness than in the other two peaks. The width of the second peak indicates an optimal and smooth surface. Peak 3 is shifted strongly to the right, since there are microcracks

on the surface that affect the average roughness parameter – the peak-to-valley height, which indicates a more complex surface morphology. On the other hand, WC films demonstrated significantly higher surface non-uniformity (Fig. 4). The differences in height have values from 100 to 500 nm. The broader and more symmetric distribution of the plots confirmed an

increase in the amount of the W₂C phase on the surface of the growing film. The change in surface morphology caused by the growth of the WC film showed that carbon alters the grain structure and increases the surface non-uniformity for all deposition rates.

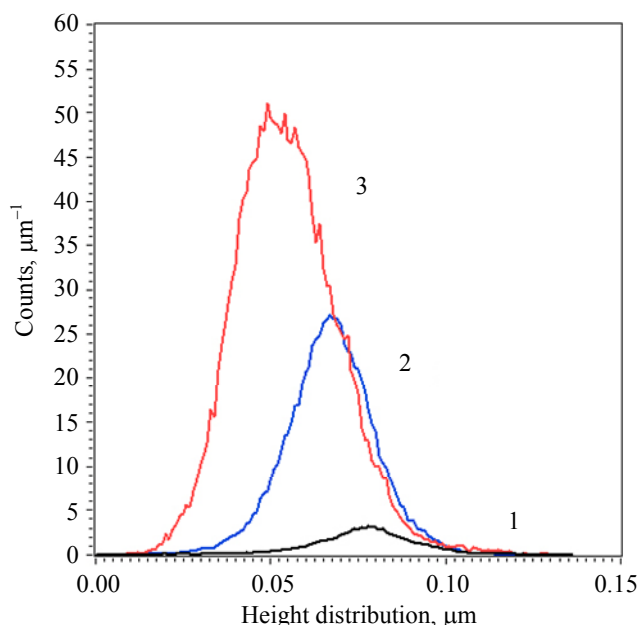


Fig. 4. Height distribution of crystallites on the surface of tungsten carbide films at three deposition rates: 1 – low; 2 – medium; 3 – high

These values additionally show differences in the symmetry and texture of the surface. WC films demonstrated more pronounced surface defects. W films are characterized by balanced

peaks and valleys, whereas for WC valleys predominate.

These results show that the addition of carbon increases the surface area and the relief of the structure of WC films, which makes them potentially more suitable for applications requiring high reactivity of surface-active substances, for example, in gas-sensitive materials or catalytic processes.

Conclusions

Thus, the work proposes and implements a method for obtaining thin polycrystalline WC films by introducing hydrocarbons with low pyrolysis energies into the plasma region and near the substrate. The method was tested on films with a thickness of 0.5 μm. The results of processing three-dimensional (3D) images obtained by AFM confirm the possibility of obtaining polycrystalline WC or WC + W₂C films in a 50:50 proportion, depending on the requirements of the experiment, by the indicated method. The possibility of controlling the "tungsten-carbon" phase composition by changing the discharge voltage at a constant direct current is shown. Further development of this method makes it possible to proceed to the study and manufacture of single-crystal films of smaller thicknesses, as well as metal-carbon films of other refractory metals.

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