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Temperature effects in nanostructured carbon-copper films deposited by magnetron sputtering

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Nanostructured carbon-copper films were deposited by direct current magnetron sputtering of composed graphite-copper or pure graphite and copper targets. The evolution of film structure on annealing in a vacuum at temperatures in the range of 300-600°C and upon deposition at 600°C has been studied by transmission and scanning electron microscopy and electron diffraction. Three types of thin annealed films were studied, namely: mixed C+Cu (type 1), two-layer C/Cu (type 2), and nanostructured (type 3). Also two types of thick films were prepared by deposition of mixed carbon-copper film onto substrate at room temperature and then annealing in a vacuum (type 4), and by deposition of mixed carbon-copper film onto pre-heated substrate (type 5).

The as-deposited films of type 1 (containing 8-22 at. % Cu) exhibited amorphous structure with copper atoms uniformly distributed over the film volume. Annealing in the range of 300-600°C resulted in precipitation of copper into the set of particles with average particle size depending on copper content and annealing temperature, and in development of diffusion coalescence within the set of particles. The coalescence occurred more slowly than it is predicted by the theory. Upon annealing at 600°C of type 2 film the copper layer disintegrated and the set of copper particles formed. The diffusion coalescence of particles also took place. Like type 1 film, in the type 2 film the coalescence occurred also more slowly than it is predicted by the theory. The structure of type 3 film was stable upon annealing at 600°C for period up to 15 h. The specific microstructure of carbon film-matrix greatly slowed down the diffusion coalescence of copper particles in the films of types 1 and 2 and prevented it in type 3 film.

Upon annealing of the film of type 4 the amorphous structure of carbon matrix preserved, and the set of copper particles formed on its surface. The film deposited onto pre-heated substrate (type 5) exhibited clearly columnar structure of carbon matrix with the set of copper particles located both in the film volume and on its surface.

Keywords: film; amorphous carbon; nanostructure; coalescence; diffusion; electron microscopy.

Наноструктурні плівки в системі „вуглець-мідь” одержані методом магнетронного на постійному струмі розпилення мішені, складеної із графіту та міді, а також чистих мішеней із графіту та міді. Еволюцію структури при відпалі в інтервалі температур 300-600°С, а також при осадженні при температурі підкладку 600°С вивчали методами електронної просвічу вальної та скануючої мікроскопії, а також електронографії. Досліджували три типи тонких плівок після відпалу, а саме; змішана C+Cu (тип 1), двошарова C/Cu (type 2) та наноструктурна (тип 3). Були досліджені також товсті плівки двох типів, одержані осадженням змішаної C+Cu плівки на підкладку при кімнатній температурі та наступним відпалом в вакуумі (тип 4), а також осадженням змішаної C+Cu плівки на наперед нагріту підкладку (тип 5).

Осаджені плівки 1-го типу (які містили 8-22 ат. % Cu) мали аморфну структуру, в якій атоми міді були розподілені рівномірно по об'єму плівки. Відпал в інтервалі температур 300-600°С призвів до виділення міді в ансамбль частинок зі середнім розміром, який залежав від концентрації міді в плівці та температури відпалу, а також до розвинення процесу коалесценції частинок. Коалесценція протікала повільніше, ніж передбачено теорією. При відпалі при 600°С плівки 2-го типу шар міді розпався і на поверхні сформувався ансамбль острівців міді. В ансамблі острівців також розвинувся процес коалесценції, який протікав також повільніше, ніж передбачено теорією. Структура плівки 3-го типу виявилась стійкою до відпалу при 600°С протягом 15 годин. Специфічна структура вуглецевої плівки-матриці істотно уповільнювала дифузійну коалесценцію в ансамблі частинок міді в плівках 1-го та 2-го типів, та заблокувала коалесценцію в плівці 3-го типу.

При відпалі плівки 4-го типу аморфна структура плівки зберігалася, і на її поверхні сформувались частинки міді. В плівці, осадженої на попередньо нагріту підкладку (тип 5), сформувалась стовпчаста структура вуглецевої матриці, а частинки міді сформувались як на поверхні плівки, та і в її об'ємі.

Ключові слова: плівка; аморфний вуглець; наноструктур; коалесценція; дифузія; електронна мікроскопія.

The ideological ground for present work is the theoretical and experimental research which was carried out under leadership of Prof. Ya. E. Geguzin at the chair of crystals physics of Kharkov university on the problem of diffusion mass transfer in discrete metal films located on the surface of real crystal.

Introduction

An interest in the composite carbon films that contain nanosized metal particles stems from the prospects in application of such films. The diamond-like (DLC) and amorphous (a-C) carbon films themselves have unique properties, such as high hardness, chemical inertness, high electrical resistance, transparency in infrared spectrum. An introduction in such films of nanosized particles opens new areas for application films, e. g. creation of the media for information recording in case of particles of magnetic material. The composite carbon/metal films are promising wear-resistant material with low friction coefficient for tribological application, and also as an electrode material for electrochemistry.

The metal-containing carbon films can be produced by different techniques, such as dc/rf magnetron sputtering,

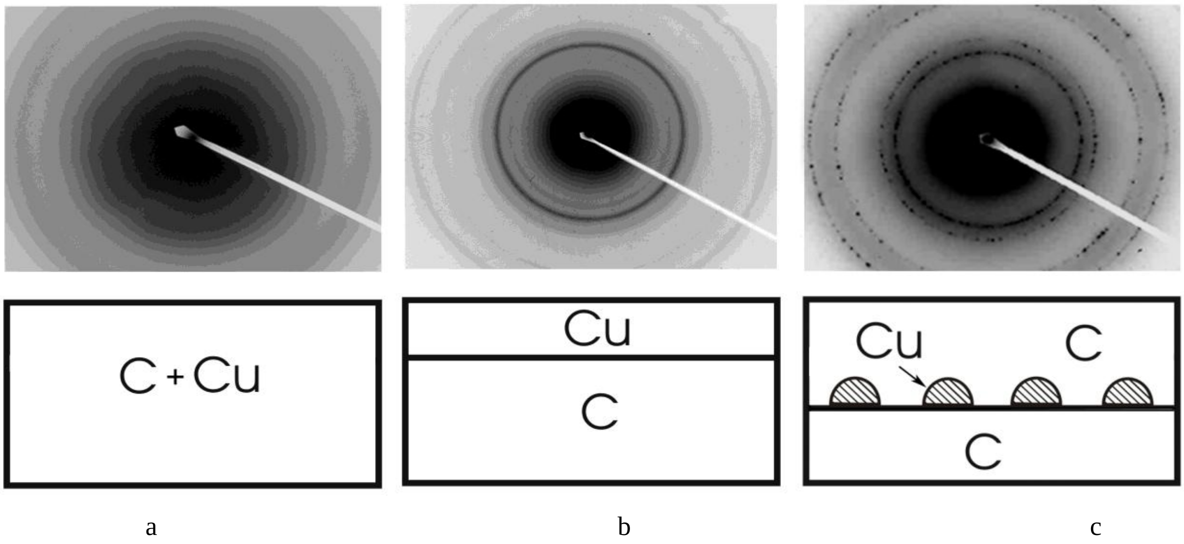

Fig. 1. Schematic representation and electron diffraction patterns of as-deposited carbon/copper films: (a) mixed (type 1); (b) two-layer (type 2); (c) nanostructured (type 3).

cathode vacuum-arc process, mass-separated ion-beam deposition, combined magnetron sputtering with chemical vapor deposition, etc [1-6]. However, when depositing carbon films the problem often arises connected with high compressive stress which tends to detach the film from the substrate when film thickness exceeds definite critical value. One of the ways to reduce the internal stress is addition of new element in the a-C matrix, e. g. the copper because it is highly ductile metal and it does not form hard carbides.

There are a number of works on the effect of copper doping on the properties of composite carbon/copper films [1, 6-10]. In Ref. [7], it was demonstrated that adding of a small amount of copper (Cu:C ratio <1:100) to a-C:H film results in an increase in the Vickers hardness and improvement of film adhesion to the silicon substrate. At the same time, in Ref. [1] the adding 11 at. % copper to a-C:H film was shown to decrease the film hardness, increase the critical load in the adhesion tests, reduce the film stress, and increase the film toughness. In Ref. [7], the optical properties of carbon/copper films have also been studied, and it was shown that copper atoms not only passivate the dangling bonds but also create a favorable environment for sp^3 structure of amorphous carbon. In Ref. [8], the hardness of a-C:H/Cu films decreased with increase in copper content up to 60 at.% while the Young’s modulus did not change. In Ref. [9, 10], the microstructure of copper nanoparticles encapsulated into carbon shell has been studied, and it was shown that the size and morphology of particles depend on the deposition and subsequent annealing conditions.

Since the carbon and copper are mutually insoluble, so to mix them it is necessary to create non-equilibrium conditions for deposition copper-containing carbon film. The magnetron sputtering technique provides with such conditions. In this chapter, the microstructure of as-deposited and annealed in a vacuum composite carbon/copper films has been studied by transmission electron microscopy (TEM) and electron diffraction (ED). The hardness of films was also measured by indentation method.

Experimental details

The carbon/copper films were sputter deposited using conventional planar balanced direct current (dc) magnetron units. The target composed from graphite disk (60 mm in diameter and 4 mm thick) and copper chips, and also pure graphite target of the same dimensions and copper target (60 mm in diameter and 1.5 mm thick) were used for film deposition. The target-to-substrate distance was 50 mm. The sputtering gas was 99.97 % pure argon at constant pressure 1 Pa. The single crystal wafers of (100) NaCl (fresh cleavages) and (100)-oriented plates of single-crystalline silicon were used as substrates. Prior to film deposition, the targets were pre-sputtered on the shield in order to remove contaminations from the target surface and stabilize the magnetron discharge parameters. The magnetrons operated at about 100 W power, and this allowed achieving of reasonable deposition rate while minimizing non-controllable heating of growing film by plasma radiation and bombardment with positive ions [11]. Under above deposition conditions, the substrate temperature during film condensation did not exceed 50°C. No biasing voltage was specially applied to the substrate during deposition.

Five types of specimens for structure study were prepared as follows. The films of type 1 were mixed C+Cu ones (Fig. 1a) deposited by sputtering of the target composed of graphite disk and copper chips attached to its surface in the sputtering zone. As substrates, the single crystal NaCl (100) plates were used. To produce the films with different copper content, the amount of copper chips was varied in different experiments. The thickness of these films was about 100 nm (for TEM and ED studies).

The type 2 film was two-layer C/Cu one deposited by successive sputtering of graphite and copper targets. In this case, the deposition rates of pure carbon (≈0.2 nm/sec) and copper (≈2.5 nm/sec) were pre-determined. The carbon layer was first deposited onto NaCl substrate for 450 sec and then the copper layer was deposited for 2 sec, so that the copper layer was 5 nm thick and the whole two-layer film specimen was near 100 nm thick (Fig. 1b).

The type 3 film was nanostructured C/Cu/C one produced as follows. A carbon layer was first deposited onto NaCl substrate for 180 sec to be about ~36 nm in thickness. Next, the copper layer was deposited onto carbon film for 2 sec to be about 5 nm in thickness. Then the carbon film with copper layer was separated from the substrate by dissolving the latter in distilled water, and placed onto a special copper mesh used in electron microscopy. This mesh material was selected because the carbon and the copper neither dissolve each other nor form carbides, and so there should not be additional doping of the film with copper during annealing. The mesh with two-layer C/Cu film was annealed in vacuum (P ≈ $1.33 \cdot 10^{-}3$ Pa) at 600°C for 1 h in order to the copper layer disintegrated into separate islands under effect of surface tension. After cooling to room temperature, the above C/Cu film was again placed in vacuum chamber and new carbon layer was deposited over the copper islands for 180 sec. As a result, the test specimen was composite C/Cu/C film of about 77 nm thick, in which individual nanosized copper particles-islands were between two carbon layers (Fig. 1c). The thickness of the layers was adjusted so that the carbon completely covered the copper particles but the whole composite film was thin enough to be examined with a transmission electron microscope.

The as-deposited carbon/copper films of types 1 and 2 were also removed from NaCl substrate by dissolving the latter in distilled water and placed onto aforementioned copper meshes. The dried meshes with films were placed in a vacuum chamber, and after pumping to a pressure of $1.3 \cdot 10^{-3}$ Pa they were annealed stepwise at temperatures 300-600°C for up to 15 h. After each annealing step and cooling to room temperature the specimens were extracted from the chamber and studied in a transmission electron microscope JEM-100CX II (JEOL) operating at 100 kV.

The specimen of type 4 was the thick carbon-copper film (like the films of type 1) deposited onto the Si substrate at room temperature, and then annealed in a vacuum ($1.3 \cdot 10^{-3}$ Pa) at 600°C for 1 h. The specimen of type 5 was the thick carbon-copper film (like the films of type 1) deposited onto the Si substrate pre-heated to 600°C. After cooling to room temperature, the surface and cross section of specimens were studied in a scanning electron microscope.

Results and discussion

Films of type 1

To study the structure evolution upon annealing of copper-doped carbon films, the specimens were prepared containing 8 to 22 at % Cu, as determined by Auger-electron spectroscopy. TEM and ED studies showed that the as-deposited films were amorphous irrespective of the copper content examined. In particular, the respective electron diffraction patterns (Fig. 1a) contained only few halos peculiar to amorphous carbon films deposited by magnetron technique under conditions identical to those used in present experiments, and TEM images did not reveal any signs of the structure. This observation indicated that the copper atoms and possibly clusters were

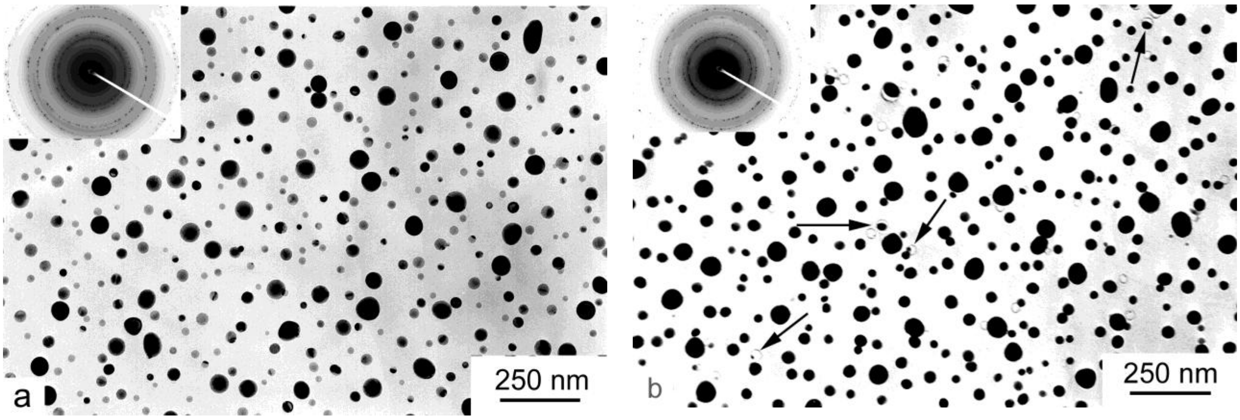

Fig. 2. TEM images and respective ED patterns taken from type 1 carbon/copper (8 at. % Cu) film after annealing in vacuum at 600°C for (a) 1 h and (b) 5 h. Arrows show the pits from partially or totally dissolved copper particles.

uniformly distributed over the volume of the as-deposited films. Annealing in a vacuum at temperatures in the range 300-600°C for 1 h drastically changed the film structure. In particular, a set of round-shaped nanoparticles formed in the film, and ED proved these to be the copper particles. The spherical shape of copper particles was clearly seen in the electron-microscopic images of the edge of film rolled up under effect of electron beam (not shown here). In Fig. 2a, the typical carbon film with copper particles after annealing under above conditions is shown.

The analysis of particle distribution with respect to their diameters has revealed that for specified copper content the average particle size in the set (determined as an average arithmetic value of diameters of all the particles involved in plotting respective size distribution graphs) decreased with increase in annealing temperature (Table 1). This sudden at first sight result will be explained further. Also, with increase in copper content in the film the average particle size in the set increased under otherwise equal annealing conditions (Table 1). This is predictable result, because it is clear that the more copper in the film, the more copper atoms will precipitate in particles during annealing.

Table 1.

Dependence of average Cu particles diameter on copper content and annealing temperature for type 1 carbon films

Cu, at. %	T_{ann}, °C	$\bar{d}$, nm
8.0	300	31.3
	450	27.2
	600	24.8
12.4	300	42.4
	450	38.3
	600	35.1
16.8	300	48.7
	450	46.5
	600	41.2
22.6	300	51.7
	450	48.6
	600	44.0

The behavior of C+Cu films upon prolonged annealing was followed with the film containing 8 at. % Cu. For this purpose, the film on a copper mesh was stepwise annealed at 600°C in a vacuum. Periodically the annealing was interrupted, and after cooling to room temperature the specimen was extracted from the chamber and studied by TEM and ED.

The size (diameter) distribution showed that after the first annealing step for 1 h the majority of particles had diameters in the range of 10-30 nm with average over the set particle diameter of 24.8 nm (Fig. 3a). The next annealing step for 1 h resulted in changes within particle set, namely the total number of particles increased somewhat, more small particles with diameters in the range of 10-30 nm and the particles with larger diameters (60-70 nm) appeared (Fig. 3b). The average over the set particle diameter became 24.5 nm. This means that not all of the copper atoms have precipitated in particles during the first annealing step (for 1 h), and this process continued in the second annealing step with formation of new particles. Some decrease in the average particle diameter is just the result of formation of additional small (10-30 nm in diameter) particles in the second annealing step. The above feature in behavior of particle set explains the observed decrease in average particle size in the film with specified copper concentration with increase in the temperature upon annealing for one-hour period (Table 1). During annealing, the copper atoms precipitate primarily at the sites which are the most appropriate for particle nucleation, i. e. on the film free surface and at structural defects, and then at sites where the probability of particle nucleation is less. The higher the annealing temperature, the higher mobility of copper atoms, and the more small particles nucleate within the first one-hour period of annealing. Therefore, the average particle size should decrease with increase in annealing temperature for films with specified copper content as it was observed in present experiments.

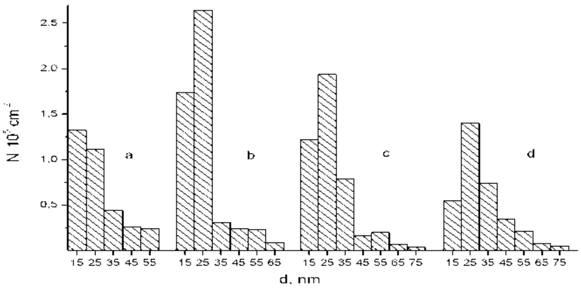

Fig. 3. Size-distribution plots for copper particles normalized for area unit of type 1 film surface after annealing at 600°C for (a) 1, (b) 2, (c) 3.5, and (d) 5 h.

Further annealing for 1.5 h resulted in the decrease in the total number of particles, in the majority of particles to have the diameters in the range of 10-40 nm with average particle diameter over the set of 26.5 nm, and also in the appearance of the particles with diameters in the range of 70-80 nm (Fig. 3c). After the next annealing step for 1.5 h, the total number of particles further decreased and the average particle size increased to 30.3 nm (Fig. 3d).

The features of histograms in Fig. 3 allowed suggestion that in the second annealing step the process of copper particles precipitation stopped and further only the process of diffusion coalescence (i. e. growth of some particles at the expense of dissolution others) within the set of particles continued. This is evidenced by the decrease in the number of small particles and in the total number of particles within the set, as well as by the increase in the average particle diameter over the set and formation of particles of larger diameters (Fig. 3c, d). The occurrence of coalescence is also confirmed by the pits free of particles and by small particles in the pits of larger size in carbon film thus indicating that some copper particles have totally or partly dissolved upon annealing (Fig. 2b).

The observed structure evolution of copper-doped carbon film can be explained based on the hetero-diffusion concept. As noted above, the copper atoms are distributed uniformly over the volume of as-deposited C+Cu films. In accordance with the results of our earlier study [11], the as-deposited at low (near room) substrate temperature carbon films consist of nanoclusters with chaotically oriented and distorted aromatic rings and graphite-like fragments within them. Subsequent annealing at temperatures up to 650°C results only in the local transformation of distorted aromatic rings into regular-shaped ones and in ordering of them within graphite-like nanoclusters in the substrate plane without increase in the size of clusters [12]. These results allowed the conclusion that the as-deposited amorphous carbon films contain large amount of structural defects, and the annealing at 650°C does not result in considerable reconstruction of the carbon film structure. Formation of copper particles can therefore be only the result of diffusion processes for copper atoms within the carbon film.

The idea of calculation of three-dimensional diffusion coalescence kinetics, i. e. variation with time of the average size in the set of particles, was first formulated in [13] in which the authors have developed a theory for coalescence within the set of inclusions in the bulk of crystal, based on the assumption that the change in inclusion radii with time is a consequence of interaction of inclusions with generalized field of atoms of inclusion substance. That field is characterized by the averaged atom concentration $\bar{\xi}$ which depends on the size distribution function $f(R,t)$ for inclusions, and it is in equilibrium with inclusions of critical radius R^*. Since near the inclusions with radius $R < R^*$ the equilibrium atom concentration is $\xi_R > \bar{\xi}$, then those inclusions have to dissolve while the inclusions with $R > R^*$ have to grow since $\xi_R < \bar{\xi}$ in this case. The average inclusion radius within the set was shown has to vary with time as $\bar{R}^3 \sim t$ [13].

Similar approach has been applied to the problem of two-dimensional coalescence in a conservative system, namely in the set of “islands” of one substance onto the surface of crystal of another substance [14]. It was shown that if the island substance mass transfer via gas phase is negligibly small compared with that over the crystal surface, then the average particle radius within the set has to increase as $\bar{R}^4 \sim t$.

As suggested above, after the second annealing step only the diffusion coalescence within the particle set occurred in type 1 films. The fact that the total amount of substance in particles, which was determined as a sum of volumes of all the particles (which was suggested to have spherical shape) within the specified surface of carbon film, i. e. $\frac{\pi}{6}\sum n_i \bar{d}_i^{\,3}$, first increased with time and after the second annealing step was virtually unchanged, allowed the assumption that the carbon-copper film under study is an analog of the conservative system considered in [13,14].

We attempted to determine the mechanism for diffusion transport of the particle substance (copper) during coalescence. Since the equilibrium pressure at 600°C for copper is negligibly low ($P = 9.78 \cdot 10^{-9}$ Pa), then one can neglect mass transfer via gas phase and consider the copper atoms diffusion occurring only within the film volume or onto its surface. In these cases, as was shown in [13, 14], the average particle radius in the set has to vary with time as $\bar{R}^3 \sim t$ or $\bar{R}^4 \sim t$, respectively. Shown in Fig. 4 is the dependence of log $\bar{R}$ on log t, from which it is evident that for annealing steps starting from the second one (i. e. when only the coalescence process is suggested to took place within the system “film-set of particles”) the tangent of slope angle for best fitted straight line is about $\frac{1}{5}$ and not $\frac{1}{3}$ or $\frac{1}{4}$ as it should be in case of diffusion only within the volume or only onto the surface of film, i. e the mass transfer occurred substantially more slowly. This finding can be explained through reasoning from the following argumentation. The results in [13, 14] were

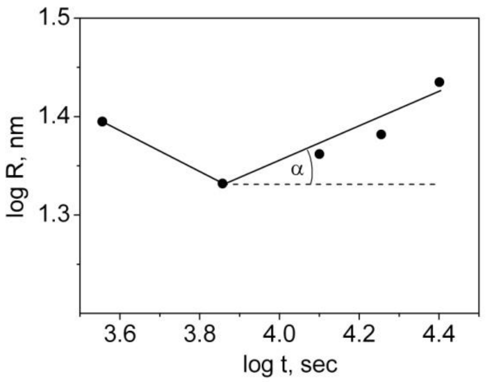

Fig. 4. Dependence of average radius of copper particles on annealing time for type 1 film.

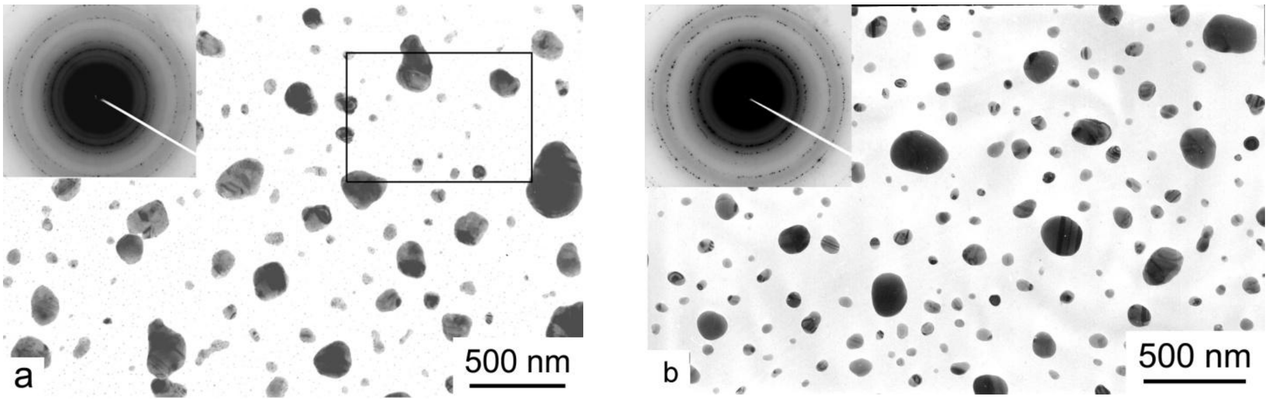

Fig. 5. TEM images and respective ED patterns for two-layer (type 2) film annealed at 600 ^{o}C for (a) 1 h and (b) 7 h.

obtained from consideration of diffusion in the spatially homogeneous medium or on atomic-smooth surface, respectively. In our case, as noted above, the as-deposited carbon film contained a large amount of structural defects that are not eliminated by annealing and hinder the diffusion transfer of copper atoms. Moreover, the pits from dissolved particles (Fig. 2b) indicate that the copper particles were partly immersed into the carbon film at different depths. So, based on above results one can suggest that the mass transport is apparently of a mixed nature, i. e. it occurs in both the film bulk and on its surface. In aggregate, all these factors determine observed by experiment the dependence of particle average size on annealing time.

Film of type 2

To elucidate the question: what is the real mechanism of mass transfer upon annealing within the set of copper particles located on the surface of carbon film, the two-layer specimen has been prepared.

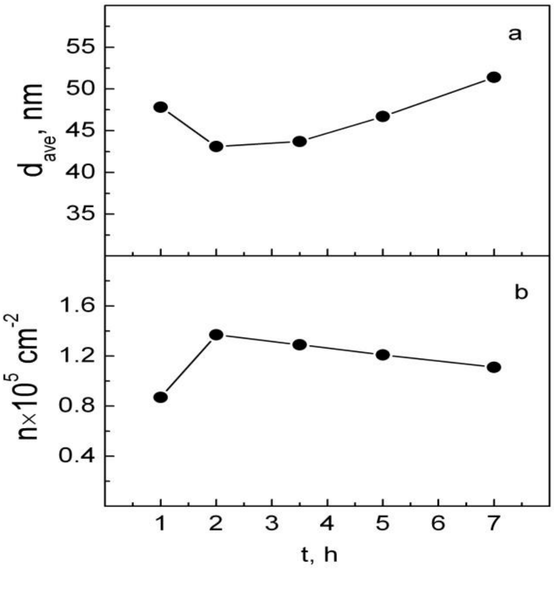

Fig. 6. Dependence of average diameter (a) and surface density of copper particles (b) on annealing time for type 2 film.

TEM and ED study of this film showed that the initial (as-deposited) film consisted of amorphous carbon layer and continuous polycrystalline copper layer (Fig.1b). Annealing in vacuum at 600^{o}C for 1 h fundamentally changed the film structure. In particular, the copper layer disintegrated due to the surface tension force and the set of particles formed on the surface of carbon film-substrate. The ED proved them to be copper nanoparticles (Fig. 5a). The particles were almost equi-axial and acquired well-defined internal structure (grain boundaries, twins, etc.). After long-term annealing the particles loss their inner sub-structure and gained more rounded shape while the carbon film remained amorphous as is evidenced by halos in ED pattern (Fig. 5b).

The behavior of the set of particles upon annealing in films of this type is also of two-stage nature like that in the films of type 1. In the first stage, after the originally continuous copper layer has disintegrated, the average size of particles decreased and their number increased during the second one-hour step of annealing (Fig. 6). Upon further annealing the diffusion coalescence developed, in particular the average diameter of particles increased and their number decreased. Since the copper layer was initially located over the carbon layer, one can assume that the particles formed as a result of copper layer disintegration are also located onto the carbon film surface. Therefore, in this case the coalescence that leads to changes in the set of copper particles seems to proceed through only the surface hetero-diffusion mechanism.

Size distribution of copper particles is of two kinds. There are particles several tens of nanometer on average (Fig. 5a) and very fine particles visible only under much higher magnification (Fig. 7). For statistical processing of TEM images the pictures should be taken under magnification that would ensure the optimum ratio between the size and number of particles. However, in this case very fine particles are not visible in the pictures, so they cannot be accounted in statistical processing, but these seem to be nevertheless involved in coalescence process. In the first stage of annealing the very fine particles coalesce due to diffusion of copper atoms and, thus, contribute to formation of additional small particles which are now accounted in statistical processing of images. Just the formation of new small particles causes the decrease in average diameter and increase in particle density in the first annealing stage comprising two one-hour annealing steps. In the second stage, the contribution from formation of small particles at the expense of finest particles becomes essentially less, and predominant is the diffusion coalescence within the set of larger particles which are accounted upon statistical processing of TEM images. As a result, the average diameter of particles increased (Fig. 6a) and the surface density of particles decreased (Fig. 6b). (Note that after prolonged annealing the finest particles disappeared and were not longer seen in electron microscopic images of particles set.)

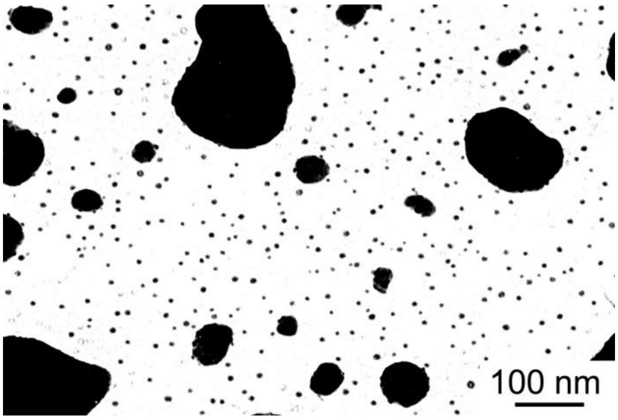

Fig. 7. TEM image with higher magnification of area shown in insert in Fig. 5a.

Analysis of the dependence of particle average diameter on annealing time ($log\,\overline{R}$ vs. $log\ t$ plot) has shown that the average radius in the set obeys again the law $\overline{R}^5 \sim t$ (like that for type 1 film) and not $\overline{R}^4 \sim t$ as it might be expected for the case of coalescence by the mechanism of surface diffusion of copper atoms [14]. We believe that deviation of the experimental coalescence law from the theoretical one is because of the real microstructure of carbon layer-substrate. As noted above, in [14] the law $\overline{R}^4 \sim t$ was derived based on the hetero-diffusion concept over the homogeneous and atomic-smooth surface. The as-deposited under conditions used in present experiments real carbon layer consists of chaotically oriented and internally strongly disordered graphite-like clusters, and that structure preserves upon annealing. So, the diffusion of copper atoms over the surface of such carbon layer seems to be hindered and therefore occurred more slowly than it is predicted by the theory.

As mentioned above, in the mixed carbon-copper films (type 1) the particles formed due to diffusion precipitation of copper atoms from the volume of carbon film. It was suggested that the process of particles set formation finished to the end of the first one-hour annealing step, and further only the diffusion coalescence of particles occurred. Based on the results obtained with films of type 2, it is now reasonable to suggest that in the type 1 films the processes of particle formation and diffusion coalescence occur simultaneously. In the first stage (two successive one-hour annealing steps) the process of particles set formation was predominant, and in the next stage predominant became diffusion coalescence of particles in the set, so that the average particle diameter increased.

Film of type 3

To verify the suggestion about surface diffusion mechanism for coalescence, the film of type 3 was examined, in which the pre-formed set of copper particles was located between carbon layers. In this case, the near

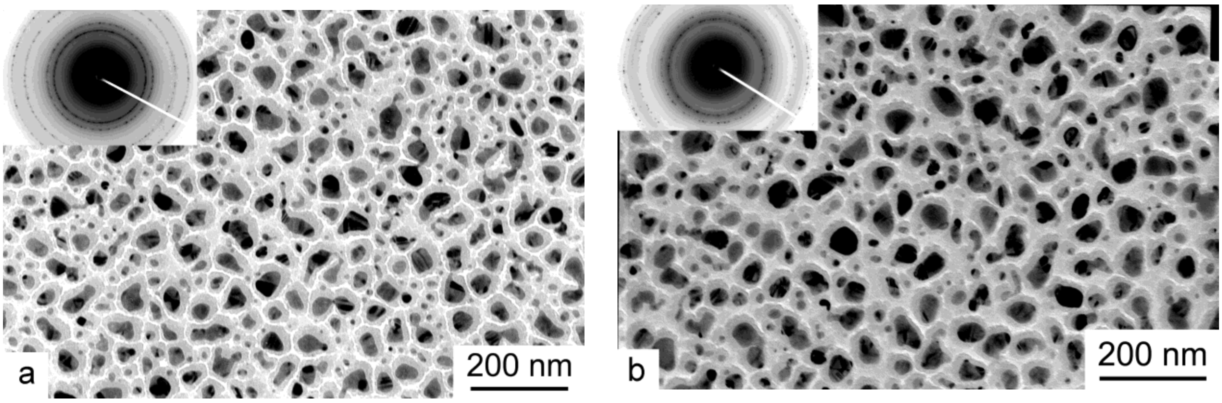

Fig. 8. TEM images and respective ED patterns for nanostructured (type 3) initial (a) and annealed at 600°C for 15 h (b) films.

regular-shaped copper particles were initially surrounded by amorphous carbon matrix thus simulating volume conditions.

Shown in Fig. 8a is TEM photograph of initial film. The copper particles gained a certain crystallographic orientation during specimen preparation annealing step, which is evidenced by the point reflections in ED pattern.

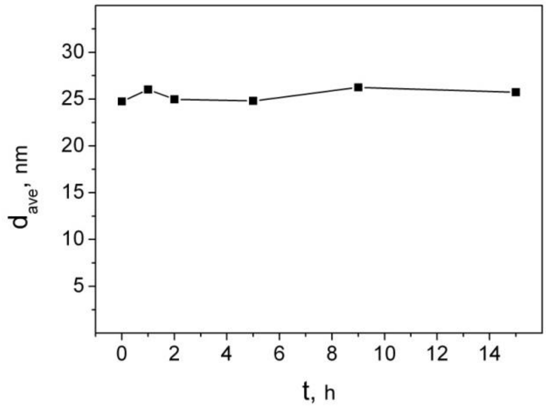

Fig. 9. Dependence of average diameter of copper particles on annealing time for type 3 film.

The coarser particles exhibit structural defects (grain boundaries, twins). Subsequent long-term annealing didn't result in any noticeable changes in the shape of copper particles (Fig. 8b).

An analysis of size distribution of copper particles has shown that the average diameter of particles was actually unchanged after annealing at 600°C even for 15 h (Fig. 9). This evidence unambiguously indicates absence of coalescence in these films, which can be explained based on aforementioned reasoning (see par. 3.1). In this case, the copper particles are surrounded by the quasi-amorphous carbon matrix with highly distorted structure which is resistant to annealing. So, the diffusion transfer of copper atoms whose size in addition is much larger than that of carbon atoms is greatly hindered because of structural imperfection of carbon matrix.

Films of types 4 and 5

The structure of annealed carbon-copper films of type 1 was formed due to the features of specimen preparation. To be appropriate for TEM study, the carbon films must be rather thin (no more than 100 nm). As was shown, the copper atoms were uniformly distributed over the carbon matrix in the as-deposited films. Since the copper forms neither solid solutions with carbon nor carbides, then upon annealing copper atoms strived to segregate into particles in order to lower the total energy of the system. Naturally, the most suitable place for particle formation is free surface of thin film, and thus the copper particle set formed just onto the carbon matrix surface with average particle diameter in the sets in the range from about 25 nm to about 52 nm depending on copper concentration in C-Cu films. However, the question remained open as to whether the copper particles form only on the carbon film surface during annealing or that process can occur also in the carbon film-matrix volume during deposition?

To give answer to above question we studied the peculiarities of structure formation in thick composite carbon-copper films in which free surface is of less importance. In view of aforesaid as to the effect of annealing on the behavior of thin carbon-copper films, we chose the highest copper content at about 22 at. % Cu and the treatment temperature of 600°C in order to ensure the film structure formation process to be the most expressive and the results comparable with those reported above for films of type 1.

Shown in Fig. 10 is the SEM image of type 4 C-Cu film deposited at low temperature and then annealed at 600°C for 1 h. It is evident that like the thin carbon-copper films of type 1, in this case the set of copper particles also formed on the film surface. The fact that these particles are metal (copper) ones is proved by the image obtained in back-scattered electrons. The estimated size of copper particles is about 120 nm, i. e. noticeably larger than for particles formed in thin type 1 carbon-copper films. This discrepancy in particle sizes can be explained based on the following argumentation. In thin film the reserve of copper is much less than in thick film due to film small volume. Upon annealing, that reserve quickly run out, and after the set of particles formed the predominantly diffusion coalescence of particles

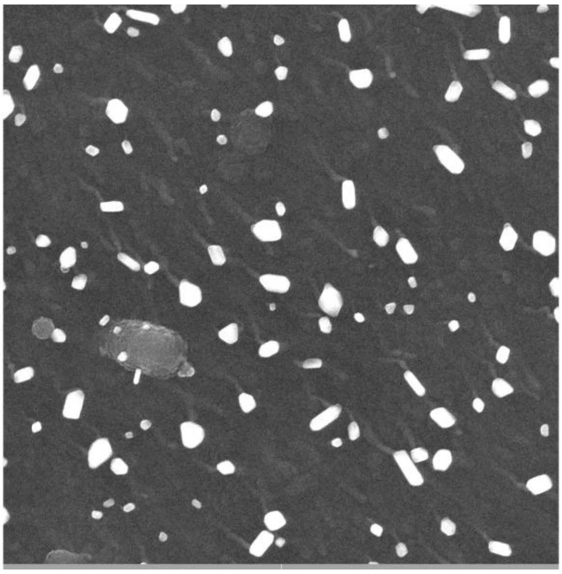

Fig. 10. Copper particles on the surface of thick type 4 carbon-copper film deposited at room temperature and annealed in vacuum at 600°C for 1 h: image in secondary electrons (left) and back-scattered electrons (right).

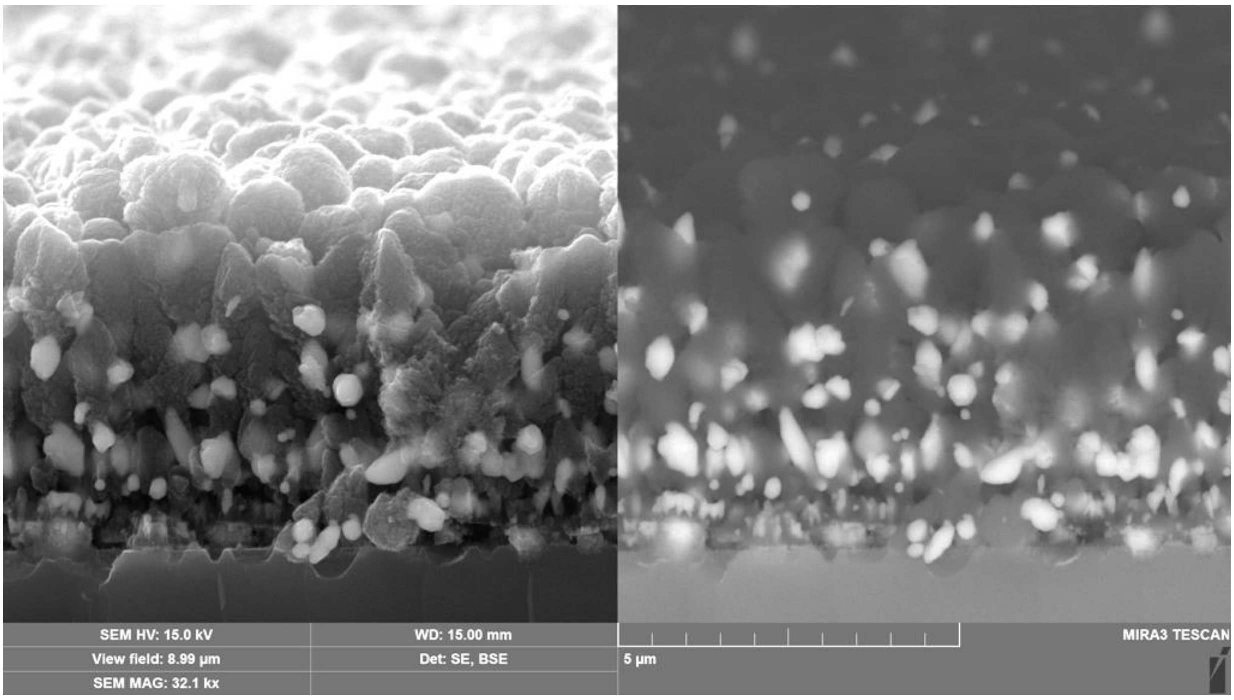

Fig. 11. SEM cross-section of thick type 5 carbon-copper film deposited at substrate pre-heated to 600^{o}C: images in secondary electrons (left) and back-scattered electrons (right).

developed. In thick film the reserve for copper is essentially larger, and more atoms are able to precipitate in particles thus resulting in greater particle size.

The following observation in the specimen cross section (not shown here) attracted attention. The film volume adjacent to the film free surface contained less amount of particles compared to deeper film volume. This observation means that the copper atoms diffused from the sub-surface layers to free film surface and precipitated there in particles. Another remarkable feature is the structure-less nature of the film. This fact is also consistent with the results in [12] where it was shown that the amorphous structure of carbon film deposited at low substrate temperature is stable to subsequent annealing at temperatures up to 600^{o}C.

The structure of type 5 carbon-copper film deposited onto the substrate pre-heated to 600^{o}C is shown in Fig. 11. The film exhibits clearly expressed columnar structure of carbon matrix. That structure agrees with the results obtained in [12], where ordering of aromatic rings and growth of graphitic clusters at deposition temperatures of ≈500^{o}C and higher was observed. Also, the copper particles formed during film deposition are distributed over the whole film volume and onto its surface. The estimated size of copper particles is about 500 nm. It is notable that particle density decreases from the bottom to the surface of film. The latter fact is consistent with the results in [15] and indicates that part of copper atoms diffused from the sub-surface carbon matrix layer and precipitated in particles onto free film surface.

Conclusions

In dc magnetron sputtering of composite graphite/copper target, the copper-doped amorphous carbon films are deposited with uniform distribution of copper atoms and clusters over the film volume. Annealing of films in a vacuum at 300-600^{o}C results in precipitation of copper particles and accompanies by changes within the set of copper particles because of diffusion coalescence. As a consequence of this, the density of copper particles decreased and their average over the set size increased. The coalescence occurred more slowly than it is predicted by the theory. With increase in copper content in the film the average particle size in the set increased with other annealing conditions being equal. With specified copper content the average particle size in the set decreased with increase in annealing temperature. The coalescence mechanism is suggested to be of mixed nature and includes the mass transfer in both the film volume and over its surface. The structure defects in carbon film reduce greatly the rate of diffusion displacement of copper atoms within the carbon film.

In the two-layer film an annealing in a vacuum at 600^{o}C resulted in two-stage microstructure evolution. In the first stage, the copper layers disintegrated into separate “islands”-particles. In the second stage, the process of diffusion coalescence developed within the set of copper particles. As a result, the density of copper particles decreased and their average size increased. The coalescence in two-layer carbon-copper film occurred also more slowly than it is predicted by the theory and obeyed the same low as for the mixed copper-doped carbon films of type 1. This is because the strongly disordered structure of carbon film preserves upon annealing at 600^{o}C and reduces greatly the rate of diffusion transport of copper atoms over the surface of carbon matrix. In the three-layer film, upon annealing the copper layer also disintegrated into particles of strongly irregular shape. The process of coalescence was not observed because of specific morphologic and structural features of copper particles and carbon layers.

In nanostructured films the average size of copper particles didn’t change upon annealing. This is because the copper particles were initially surrounded with carbon matrix whose real structure effectively hindered the diffusion transfer of copper atoms and thus prevented the coalescence of copper particles by volume diffusion mechanism. So, the results obtained with types 1 to 3 carbon/copper films make it possible to conclude that upon annealing the mass transfer within the set of copper particles occurs predominantly by the surface hetero-diffusion mechanism.

The thick carbon-copper film deposited at low temperature and then annealed at 600^{o}C for 1 h preserved the amorphous structure of its carbon matrix, and the set of copper particles formed onto its surface. The film deposited onto pre-heated to 600^{o}C substrate exhibited well-defined columnar structure of carbon matrix with the set of copper particles in the film volume and onto its surface. The substrate temperature during deposition and/or post-deposition annealing is critical for copper precipitation both in the carbon film volume and on film surface.

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