

Metal-fullerene on materials for electronics

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The results of studying the physical properties of film materials containing metals and fullerenes are presented. It is shown that the use of these materials in electronics, optoelectronics, biomedicine significantly increases the capabilities of tools and mechanisms.

INTRODUCTION

Fullerenes are unique carbon nanoparticles. The molecules of C₆₀ fullerenes, due to the high symmetry and closure of all σ bonds, have high stability (up to 1700 K in an inert medium), can attach up to 6 free electrons, in addition to the formation of chemical compounds, external molecules can interact with different atoms (creation of endohedral fullerenes). The adiabatic affinity to the electron in the solution is 2.1-2.2 eV [1]. The fullerene C₆₀ molecule can receive up to 12 electrons [1,2] and give up one electron [3], i.e. the charge on the C₆₀ molecule can vary from +1 to minus 12. The polarizability of the C₆₀ fullerene molecule is large ($\sim 85 \text{ \AA}$) by several times the polarizability of the molecules of other acceptors. Therefore, polarization van der Waals forces play an important role in the formation of donor-acceptor complexes and ion-radical fullerene salts. Important physiological results have been obtained by physicists, chemists, materials scientists, biologists and physicians since the discovery of fullerenes, a number of different applications of materials containing fullerenes have been proposed and implemented [1-5].

In this paper we present the results of studying the physical properties of film materials containing metals (Au, Ag, Cu, Ti, Fe, Sn, Ga) and fullerenes. It is shown that the use of these materials in electronics, optoelectronics, biomedicine, significantly increases the capabilities of instruments and mechanisms.

EXPERIMENTAL DETAILS

The formation of metal-fullerene materials from a combined atomic-molecular flow in vacuum was

carried out in three stages: 1) degradation of the starting materials; 2) delivery of building components to the substrate; 3) the structuring of the film on the substrate. The formation of new phases. Over the past 15 years, with the participation of the authors of this work, various methods for obtaining new types of nanostructured metal fullerene materials have been developed and their physical and physicochemical properties have been studied. The simplest way of obtaining materials based on metals and fullerenes is evaporation and their joint condensation in a vacuum. This method provides high purity of materials, control of the structure and concentration of condensates, it is easy to implement on standard vacuum equipment, does not require large quantities of raw materials. Since the fullerenes begin to sublime at temperatures below 700 K, and the evaporation temperatures of most metals are more than 1200 K, two evaporators were used to obtain combined atomic-molecular fluxes. The studies carried out show that materials containing fullerenes have special mechanical, tribological, optical, sorption properties, often combining in one material incompatible properties (for example, low density with high strength, high adhesion and low coefficient of friction, high strength and high plasticity).

The production of films with different contents of fullerenes was provided by varying the densities of the atomic cluster flows of the components, which in turn was achieved by adjusting the temperature of the evaporators and changing their location relative to the substrate. The real concentration of fullerenes in metal-fullerene films was determined by X-ray microanalysis using the intensity of characteristic X-ray radiation, taking into account the thickness of the films and coatings.

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As raw materials, especially pure metals were used: copper, aluminum, tin, titanium (not worse than 99.99), and fullerite powder C_{60} of 99.9% purity, manufactured according to the previously described [6] technology. Substrates were oxidized silicon and steel. The annealing temperature was 470 and 670 K.

The phase composition of the samples was monitored on a diffractometer "DRON 3.0" in copper K radiation using an automation system based on a personal computer that includes all the functions of controlling the goniometer. The structure and elemental composition of the samples was investigated with a scanning electron microscope LEO 1455 VP at an accelerating voltage of 20 keV. The structure of some samples was investigated using an atomic force microscope (AFM). Measurement of electrical characteristics was performed by resistometric methods using low-resistance and high-resistance potentiometers. Friction coefficients were determined with a TEU-2 tribometer, volumetric wear was calculated from the depths of grooves of the friction path measured by the interferometric method (Linnik interferometer, MI-4).

RESULTS AND DISCUSSION

The mechanical, tribological, optical, sorption properties of composite materials based on fullerene molecules and metal atoms are directly related to the surface interaction of the contacting phases. It was found that fullerenes are not only stable nanoparticles, which change the properties of the material due to its presence as a filler component of the composite material, but acts as an instrument for influencing the structure of the bond matrix, as a stimulator of synergistic structuring processes.

It is established that a condensation in a vacuum of a metal (for example, copper, aluminum) and fullerene C_{60} forms an ultradisperse structure with a particle size of 10 ... 80 nm. It is shown that the structure of metal-fullerene films depends on the technological conditions of their production: the substrate temperature, the condensation rate, the effects on the atomic-molecular flow in the reactor space on approach to the substrate. In this case, heterophase films under the same condensation conditions have smaller dimensions (10-40 nm) of

the structure elements in comparison with homophase films.

Using vacuum technologies, layers of fullerite with fcc and hcp structures, metal-fullerene layers with heterophase structure possessing metallic and semiconductor properties have been obtained with the participation of authors [6-8]. For some compositions of metal-fullerene layers ($Cu-C_{60}$, $Sn-C_{60}$), the formation of chemical compounds (Cu_6C_{60} , Sn_xC_{60}) has been established [9]. Note that copper and tin with atomic carbon do not form chemical compounds, and their mutual solubility is negligible.

Endohedral fullerenes are of great interest. Since the inner diameter of the fullerene shell is much larger than the diameter of the encapsulated atom, when the valence electrons are transferred to the outer surface of the fullerene shell, the equilibrium position of the encapsulated atom shifts relative to the geometric center of the fullerene shell. This determines the presence of a sufficiently large constant dipole moment for such molecules. Such crystals must have anisotropic properties and can find interesting applications in electronic devices. The restructuring of the electronic structure of the endohedral complex leads to the fact that the metal atoms transmit, partially or completely, their valence electrons to the outer part of the fullerene shell, practically losing their chemical identity. The transition of the valence electrons of the metal to the outer shell is reflected in such electronic characteristics of the molecules as its ionization potential and electron affinity [10, 11].

Nonlinear optical effects in fullerene-containing materials (third harmonic generation, limiting the intensity of the outgoing radiation, as well as a magneto-optical effect consisting of a decrease in microhardness (an increase in plasticity) under the action of a magnetic field are established [12, 13].

Diamond-like films are obtained from fullerenes with a coefficient of friction of 0.01. The coefficient of friction between steel surfaces is reduced to values of 0.1 ... 0.2 when fullerenes are added to the boundary grease [14].

Specific features of diffusion in metal-fullerene layers, which are a high migration rate of metal atoms compared with the migration rate of C_{60} molecules, and an increase in the metal concentration (in particular, copper for the $Cu-C_{60}$

system) in the near-surface layer are established [15].

Metal-fullerene materials have the widest range of physical and physical-chemical properties. The introduction of fullerenes into materials, even in small fractions (up to 1.0 wt.%), Significantly (in some cases, at times) alters their physical and physico-chemical properties. However, for

electronics, electrical and optical properties and their variation under various influences (temperature, pressure, radiation, adsorption, etc.) are most important.

The table shows the systems we studied, the concentration and temperature intervals, and the limits of the values of certain characteristics of metal fullerene films.

Table 1. The studied systems, temperature intervals and limits values of some characteristics of metalfullerene films.

Systems	Compositions n_M / n_{C60}	R, Om	$\rho \cdot 10^3$, Om-sm	Coefficient. Friction, μ	Temperature Intervals, T, K
Ti-C ₆₀	2-200	3.5 – 260	200-3.0	0.32	293-593
Fe-C ₆₀	10-100	9.0 – 210	180-2.0	0.22	293-593
Cu-C ₆₀	2-150	3.0 – 220	150-1.5	0.37	293-493
Sn-C ₆₀	2-150	5.0 - 360	200-3.0	0.25	293-493
Ga-Ag-C ₆₀	1:1:1	5.0	$5.0 \cdot 10^{-5}$	0.35	273-393
Ag-C ₆₀	0.01	5.5	$5.4 \cdot 10^5$	0.28	293-493
Au-C ₆₀	0.01	6.2	$6.0 \cdot 10^5$	0.24	293-493

The specific electrical resistivity at the direct current of metal-fullerene films (if no new phases are formed) can vary within the limits of the values of the resistivity of the metal and fullerite. The interaction of C₆₀ molecules with one another and with metal atoms can lead to the appearance of ordered structures. In this case, phase inclusions can significantly change the form of the concentration dependence of the specific electrical resistivity of fullerene-containing films.

Values of the coefficient of strain resistance of metalfullerene composites are several times higher than the values for platinum, which is the most effective and often used for tensometry. Figure 1 shows the dependence of the coefficient of strain resistance and the resistivity on the ratio of the number of titanium atoms to the number of fullerene molecules in the alloy.

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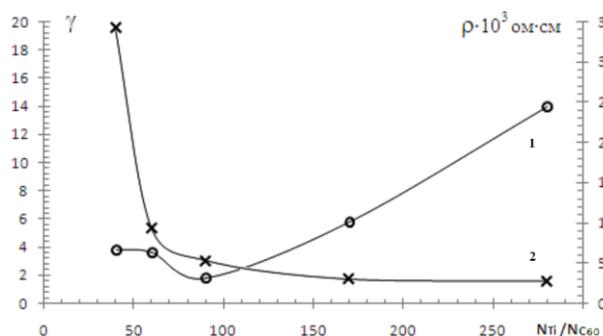


Fig. 1. Change in the coefficient of sensitivity of γ (1) and specific electric resistance ρ (2) from the fractional ratio n_{Ti} / n_{C60} of the components of titanium-fullerene films.

The electrical resistance of the alloys when measured with alternating current depends on the frequency, which indicates the presence of a capacitive component of the electrical resistivity. Figure 2 shows the dependence of the electrical conductivity of Cu-C₆₀ films on the composition of the components measured at different frequencies.

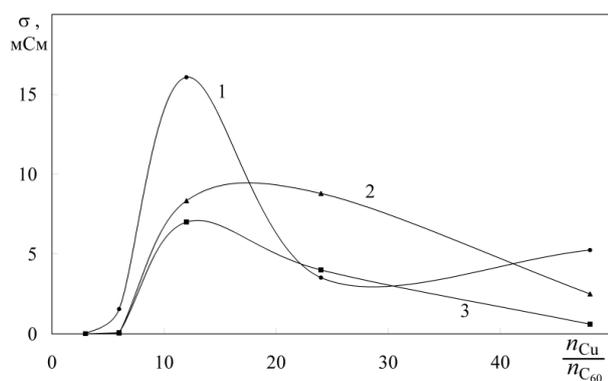


Figure 2. Dependence of the electrical conductivity of Cu-C₆₀ films on different frequencies of alternating current from the calculated number of copper atoms per molecule of C₆₀: 1 - 1 MHz; 2 - 10 kHz; 3 - 100 Hz.

An increase in the fraction of fullerite nanoparticles in the metal fullerene structure for alternating current entails a change in the value of both the capacitive and resistive components of the electrical resistivity.

A new titanium-fullerene material is obtained, which exhibits the properties of R-C-L-chains at alternating current. On the basis of this material, a high-pass filter has been developed, for which the position of the minimum electrical resistance on the frequency dependence is determined by the proportional ratio of titanium and fullerite [16].

Fullerenes, complexes of fullerenes with other atoms and molecules are promising components for the formation of optoelectronic systems and elements possessing unique electrical and optical properties. Such structures will not only increase the speed, the density of information recording, reduce the dimensions of devices, reduce the power consumption, but will also solve a number of fundamental problems (for example, the high stability of fullerenes and fullerene-like formations will solve the problem of degradation of the properties of structures with time, and will allow creating fundamentally new electro- and optomechanical devices). The fullerenes and fullerene-like particles introduced into the metal matrix can form functional optoelectronic devices of nanometer dimensions, including those with superconducting properties.

CONCLUSION

To date, many ideas have been voiced to create memory devices with a high data recording density. Active development of new types of devices based

on the principles of quantum mechanics (for example, one-electron transistors).

Perhaps non-lithographic construction of cellular ordered nanometric-sized structures on the basis of islet films or fullerene clusters in lipid matrices. Porous oxides (for example, Al₂O₃) can also serve as the basis for the formation of fullerene-containing nanosized cells that have new optical and electronic properties.

The presented results of the investigation of the properties of film materials containing metals and fullerenes allow us to conclude that the use of these materials in electronics, optoelectronics, biomedicine, significantly increase the capabilities of instruments and mechanisms.

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