Surface Morphology and Nanohardness of Fullerite–Aluminum Films

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Abstract—The surface morphology, elemental composition, and nanohardness of thin fullerite–aluminum films with different atomic fractions of metal are investigated by scanning electron and atomic-force microscopies, X-ray spectral microanalysis and nanoindentation. The films are obtained by the method of resistive evaporation in vacuum from a combined atomic-molecular flux of Al atoms and C60 molecules on single-crystal silicon substrates with the surface orientation (111). It is established that during deposition on unheated substrates, a nanocrystalline structure of films with an atomic fraction of metal of 20, 25 and 35%, with an average size of structural elements of 10, 15, and 25 nm, respectively, is formed. At the same time, internal mechanical stresses arise in the films, the relaxation of which leads to the exfoliation of significant sections of the film. During the deposition of films on substrates heated to 420 K, films with an average size of structural elements of 50–100 nm without exfoliation are formed, but in this case the nanohardness of the films decreases compared to the films obtained on unheated substrates.

Keywords: fullerite–aluminum films, atomic-force microscopy, internal mechanical stresses, surface morphology, nanoindentation, phase composition, exfoliation of films
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INTRODUCTION

Aluminum alloys have found broad application in various fields of science and technology: space and aviation industries, instrument making, mechanical engineering and others. To improve the physical and mechanical properties of aluminum-based composite materials, alloying additions of carbon phases are introduced into the metal matrix [1–8]. For example, it was established in a number of works [2–6] that the addition of fullerenes to aluminum leads to a decrease in the grain size, an increase in the microhardness of the composite due to the formation of covalent bonds and grain-boundary hardening, and a decrease in density compared to pure aluminum due to the low density of the fullerite phase (1.72 g/cm³). In [9–12], fullerite–aluminum composite materials synthesized at a high pressure also showed improved mechanical characteristics. The authors of [13] investigated the electrical conductivity of nanofragmented aluminum modified with different mass fractions of fullerene C60, and the possibility of optimizing its electrical and mechanical properties is shown. The proposed shell model of the structure made it possible to estimate the electrical conductivity of such a material.

The improvement of existing materials and development of new materials based on aluminum is still an urgent task of modern materials science. It was found in [14, 15] that the doping of fullerite with aluminum atoms up to 10% leads to improvement in the physical-mechanical properties of the composites.

The aim of this work is to study the surface morphology, elemental composition, and nanohardness of fullerite–aluminum films with a high metal content (≥20 at.%).

EXPERIMENTAL

The films were obtained by thermal evaporation in vacuum on a VUP-5M installation. From a combined atomic-molecular flow, a C60–Al film was deposited onto unheated and heated substrates (to $T = 420$ K) made of oxidized single-crystal silicon with the surface orientation (111). The atomic fraction of metal in the films was 20, 25, and 35%, and the thickness of the films was 600 nm.

The structure and elemental composition were studied using a LEO 1455 VP scanning electron microscope (Carl Zeiss, Germany) and an Aztec Energy Advanced X-Max 80 energy dispersive nitrogen-free spectrometer (Oxford Instruments,
England). The surface morphology was studied using a Solver P47 Pro scanning probe microscope (NT-MDT, Russia) in the amplitude-frequency modulation mode by the constant force method [16]. We used silicon probes with a radius of curvature of the needle tip of 1–3 nm. The nanohardness of the samples was determined by the nanoindentation method [17] using a Shimadzu DUH-202 ultramicrohardness tester. A three-edged Berkovich indenter was used. On each sample, ten imprints were carried out at a distance of

Fig. 1. AFM images of C$_{60}$–Al films with different atomic fractions of metal, deposited onto substrates not heated (a, c, d) and heated to $T = 420$ K (b, d, f): (a, b) 20 at % Al; (c, d) 25 at % Al; (e, f) 35 at % Al.
at least 50 μm from each other with a load on the indenter of 5 mN. The error in measuring the nanohardness did not exceed 10%.

RESULTS AND DISCUSSION

During the deposition of fullerite–aluminum films with different atomic fractions of metal, both on unheated and heated substrates (to \( T = 420 \) K), a nanocrystalline structure is formed. It was found by atomic-force microscopy that with an increase in the atomic fraction of aluminum, the size of structural elements in the films deposited onto an unheated substrate increases and amounts to 10, 15, and 25 nm in fullerite–aluminum films with an atomic fraction of metal of 20, 25, and 35%, respectively (Figs. 1a, 1c, 1e). When films are deposited onto heated substrates, the size of structural elements also depends on the atomic fraction of aluminum and is 50, 65, and 100 nm in fullerite–aluminum films with a metal atomic fraction of 20, 25, and 35%, respectively (Figs. 1b, 1d, 1f). An increase in the size of structural elements with an increase in the aluminum concentration is due to an increase in the deposition time of the films. To obtain films of the same thickness and a uniform distribution of aluminum over the thickness of the film, the rate of metal-atom supply for all concentrations was maintained constant; accordingly, the deposition time of the film increased with a higher Al content, which contributed to enlargement of the nucleation centers. Film deposition onto a heated substrate increases the mobility of \( C_{60} \) molecules and Al atoms entering the substrate, which also leads to the growth of large particles.

The method of X-ray spectral microanalysis revealed that aluminum is uniformly distributed in fullerite films at all investigated metal concentrations (Fig. 2).

Analysis of the surface morphology of fullerite–aluminum films deposited onto unheated substrates showed the presence of separate exfoliated areas in the form of swollen zigzag shapes. The degree of exfoliation depends on the atomic fraction of the metal. Figure 3 shows that an increase in the aluminum concentration in the fullerite films leads to an increase in the area of the exfoliated sections. The presence of swollen areas indicates the relaxation of compressive internal mechanical stresses in the films caused by mismatch of the parameters of the face-centered cubic lattice of aluminum (\( a = 0.40494 \) nm) and the hexagonal close-packed lattice of fullerite (\( a = 1.002 \) nm, \( c = 1.638 \) nm), structural defects, as well as the incorporation of aluminum atoms into the fullerite lattice and the formation of the nuclei of new phases. The formation of heterophase structures in fullerite–metal films was also found during the codeposition of \( C_{60} \) and atoms of tin and bismuth in works [18, 19].

Upon the condensation of fullerite–aluminum films with different atomic fractions of the metal onto heated substrates (to \( T = 420 \) K), a nanocrystalline structure is formed without exfoliation. Heating the substrate increases the adhesion of the film to the substrate and decreases structural defects.

It was established by the nanoindentation method that the nanohardness of fullerite–aluminum films obtained from a combined atomic-molecular flow on unheated substrates made of oxidized single-crystal silicon barely changes with a variation in the atomic fraction of aluminum in the films from 20 to 35% (Fig. 4) and averages 1.45 GPa, which is much higher than the nanohardness values for pure fullerite (0.86 GPa) and aluminum (0.32 GPa) films. Grain-boundary hardening is associated with the small grain size of the materials under study, as well as internal mechanical stresses arising at the interface between the layers. When films are deposited onto heated substrates, the nanohardness of the samples decreases by almost 40%, which can be explained by an increase in the size of structural elements and the partial relaxation of internal mechanical stresses.
In fullerite–aluminum films with a metal atomic fraction of 20, 25, and 35 at % obtained in vacuum from a combined atomic-molecular flux of metal atoms and C$_{60}$ molecules on substrates of oxidized single-crystal silicon, a nanocrystalline structure is formed with an average size of structural elements of 20–100 nm and increased nanohardness in comparison with pure films of fullerite and aluminum. When the films are deposited onto unheated substrates, compressive internal mechanical stresses arise in the films, the relaxation of which leads to the exfoliation of individual sections of the film. The deposition of films onto heated substrates (to $T = 420$ K) results in a film without exfoliation.

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