

Spontaneous growth of petal crystals in fullerite films

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Changes in the structure, elemental and phase compositions of fullerite films after their storage in air are investigated by scanning electronic microscopy, atomic force microscopy, X-ray spectroscopic microanalysis, X-ray diffraction, and Raman spectroscopy. The formation of the petal and flower-like fullerite crystals under the action of internal stress is established.

Keywords: fullerite, petal crystals, films, structure.

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1. Introduction

Fullerenes are unique objects with interesting physical and chemical properties. In the condensed condition, fullerenes form a molecular crystal – fullerite, whose crystallographic symmetry depends on many factors: method of production, type and substrate temperature of heating on which molecules are adsorbed, deposition rate, etc. C_{60} fullerite crystals, grown at room temperature from a solution by the salting-out method, usually have face-centered lattice [1], in which molecules rotate, as interaction forces between molecules are small, and the symmetry degree is very high [2]. At 260 K the transition into a primitive cubic lattice occurs with simultaneous partial freezing of the molecular motion, owing to increased intermolecular interaction. During the process of the fullerite films producing, the crystal structure with a hexagonal close-packed lattice [3] can be formed from a gas phase.

In previous works [4–8] research was presented for the structure dependence of deposited fullerite C_{60} layer from a substrate type, where monocrystal silicon, metals, highly oriented pyrolytic graphite, substrate heating temperatures were usually used. The structure of the fullerite films is determined both by the technological spraying parameters, including vacuum level, sublimation speed, distance of the evaporator to substrate holder, heating temperature and type of the substrate on which the film is to be deposited. To use this structure in actual practice, the time properties stability of the received films is important, which is to a great extent determined by the stability of structure. However, there are, virtually, no facts in the literature about the structure evolution of the fullerite films over time.

The purpose of work is research of the changes of the crystal fullerite films C_{60} structure grown onto silicon substrates that occur after storing samples in air.

2. Experimental

Fullerite films were prepared by successive chemical vapor deposition in a VUP-5M system in vacuum no worse than $1.3 \cdot 10^{-3}$ Pa. As a feedstock, C_{60} powder with purity greater than 99.98 % was used. C_{60} molecules were deposited onto the oxidized single-crystal Si (111) wafers. Fullerenes were sublimated from a tantalum crucible, whose temperature was maintained at $T = 770$ K. This value ensured a high deposition rate for the films (2 nm/s).

The synthesized films had a thickness 350 nm. The surface morphology was analyzed using a Solver PRO-P47 atomic force microscope in contact mode. We used ultrasharp silicon cantilever probes with a tip radius in the range 1 – 3 nm.

The phase composition of the films was determined by X-ray diffraction on a Rigaku Ultima IV multipurpose X-ray diffractometer with $CuK_{\alpha 1}$ radiation in Bragg–Brentano geometry (intensity data were collected using a Rigaku ultrasensitive, highspeed, multichannel detector, which allowed us to obtain X-ray diffraction patterns of thin layers). The film structure was investigated under an LEO-1455 VP scanning electron microscope at accelerating voltages of 15 kV. Distribution of elements in the films was obtained by X-ray microanalysis using an Aztec Energy Advanced X-Max 80 nitrogen-free energy dispersive microanalyzer (123-eV energy resolution for MnK_{α}) during electron beam scanning along the linear direction. Spectra of combination scattering at a fixed resolution (1 cm^{-1}) were registered at room temperature using a Nanofinder High End (Lotis TII, Belarus–Japan)

confocal-microscope-based setup. To start excitation of a sample, the laser radiation with a $\lambda = 473$ nm was applied. The laser capacity was weakened through the use of filters to values less than 0.5 W/cm^2 . The choice of low capacity laser energy is required in order to avoid photoinduced changes or heating of the samples.

3. Results and discussion

The structure and phase composition of C_{60} powder used for spraying are illustrated in Fig. 1. The powder appears as crystallites with an average size $150 \mu\text{m}$, possessing face-centered cubic lattice ($a = 1.4115 \text{ nm}$), sp. gr. Fm3m. It was established by atomic-force microscopy that the as-prepared fullerite films onto the substrates of the oxidized monocrystal silicon have homogeneous granulated structure at an average granular size of 80 nm (Fig. 2a).

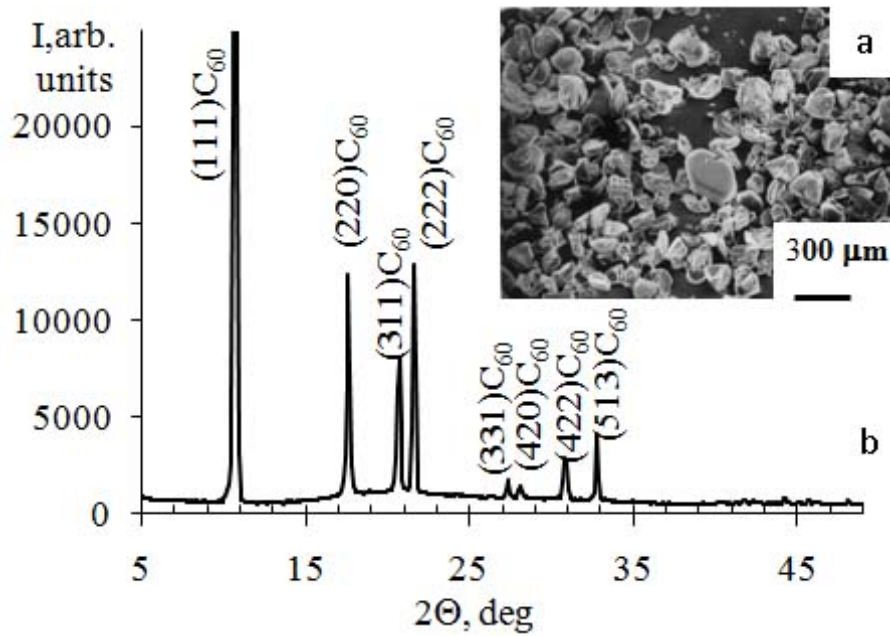


FIG. 1. The structure (a) and X-ray diffraction pattern (b) of C_{60} powder

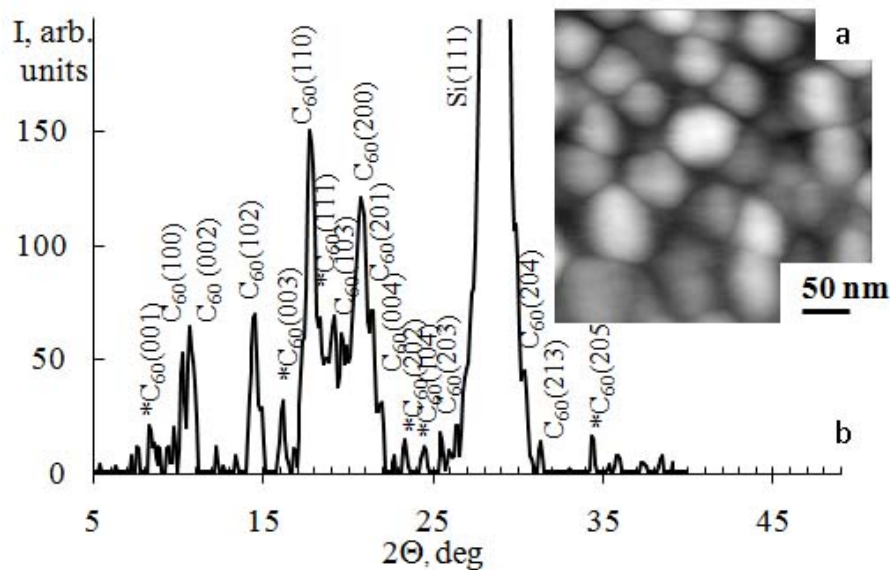


FIG. 2. The AFM-image (a) and X-ray diffraction pattern (b) as-prepared C_{60} fullerite films

By the method of X-ray diffraction, it was established that during the process of condensation onto the silicon substrate of C_{60} molecule one is forming the crystal structure with hexagonal close-packed lattice ($a = 1.0020$ nm, $c = 1.6381$ nm), sp. gr. $P6_3/mmc$ (Fig. 2b). There are a number of lines of low intensity in the XRD patterns, which are also visually displayed on the theory of the hexagonal system ($a = 1.0020$ nm, $c = 1.6162$ nm), sp. gr. $P6/mmm$. The transformation of the fcc into an hcc lattice occurred as a result of the high deposition rate of C_{60} molecules (2 nm/s) onto the non-heated substrate, as a result of which the nanocrystal film was formed. Halo presence in the angles area of 17 – 22 degrees is caused by X-ray amorphous clusters of C_{60} molecules in size of up to 10 nm that are present in the films, which have been found out in the work [9].

Figure 3 shows Raman spectra of C_{60} film. The spectrum contains all the 10 vibration modes (the pentagonal pinch $A_g(2)$ mode, two “breathing” A_g – the modes conformed to symmetric fluctuations of entire molecule (492.3 cm^{-1}) and pentagons (1464.2 cm^{-1}) and 8 H_g -mode), active in Raman spectroscopy, which testifies the purity and uniformity of the film.

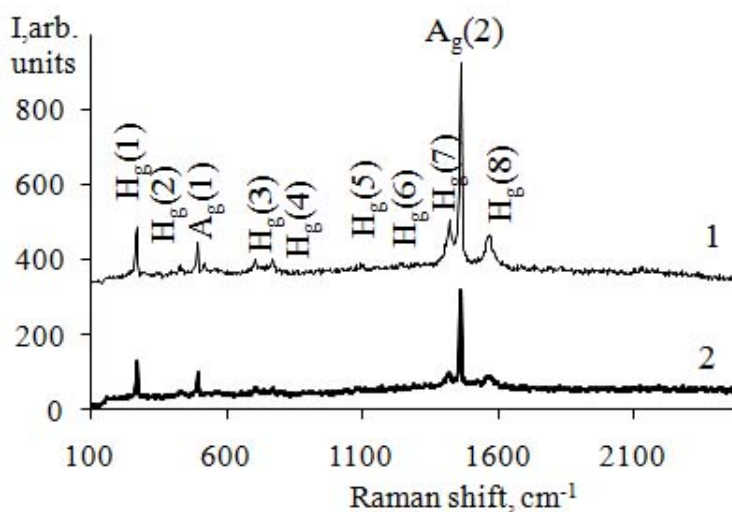


FIG. 3. Raman spectra of C_{60} films: 1 – as-prepared; 2 – after storage in air within 30 months

After long-term aerobic storage in the desiccator (30 months), petal and flowerlike formations were found on the surface of fullerite films (Fig. 4). By the method of atomic-force microscopy it was established that petal formations have thickness of 50 – 500 nanometers, with that their length changes from units to several tens micrometers. For the element structure specification of petal formations X-ray spectroscopic microanalysis was carried out. Electronic beam scanning of the lined AB-direction showed that this formation consists of carbon (Fig. 5).

Due to the developed surface morphology, the fullerite phase line's intensity decreases fractionally on X-ray pattern of the films; new phases are not revealed. There are vibration modes C_{60} on the Raman light dispersion spectrum in the flower-like formation.

It is known that whisker crystals of metals with low melting temperature (Sn, Cd, Zn, Sb, In, etc.) can grow on thin metal layers without any foreign action at room temperature. Fullerite is a crystal with a low sublimation temperature (650 K); therefore, spontaneous growth of whisker fullerite crystals may occur at room temperature.

Spontaneous growth of whisker crystals is characterized by the existence of a long-term incubation period. Under ordinary conditions, the growth depends on the sublayer on which a coating was deposited.

Spontaneous growth of whisker crystals is based on the dislocation mechanism. Internal stress is the energy source. This energy source is internal stresses, which arise in the fullerite films as consequence of parameters discrepancy of the contacting materials lattice and structural defects. Growth in the form of thin petal crystals can be caused by helical sources, emerging to two mutually perpendicular surfaces. Petals crystals develop either through overgrowth of bridges between neighboring parallel whisker crystals or via expansion of prismatic faces to opposite sides.

Unintentional atomic or molecular impurities adsorbed on the end faces of whisker crystals can also stimulate the expansion of faces, as a result of which, the layer-by-layer or chain formation of faces occurs without hindrances. Thus, petal microcrystals are formed through anisotropic lateral growth of whisker crystals playing a leading role. Interaction between petal crystals leads to the development of flowerlike formations.

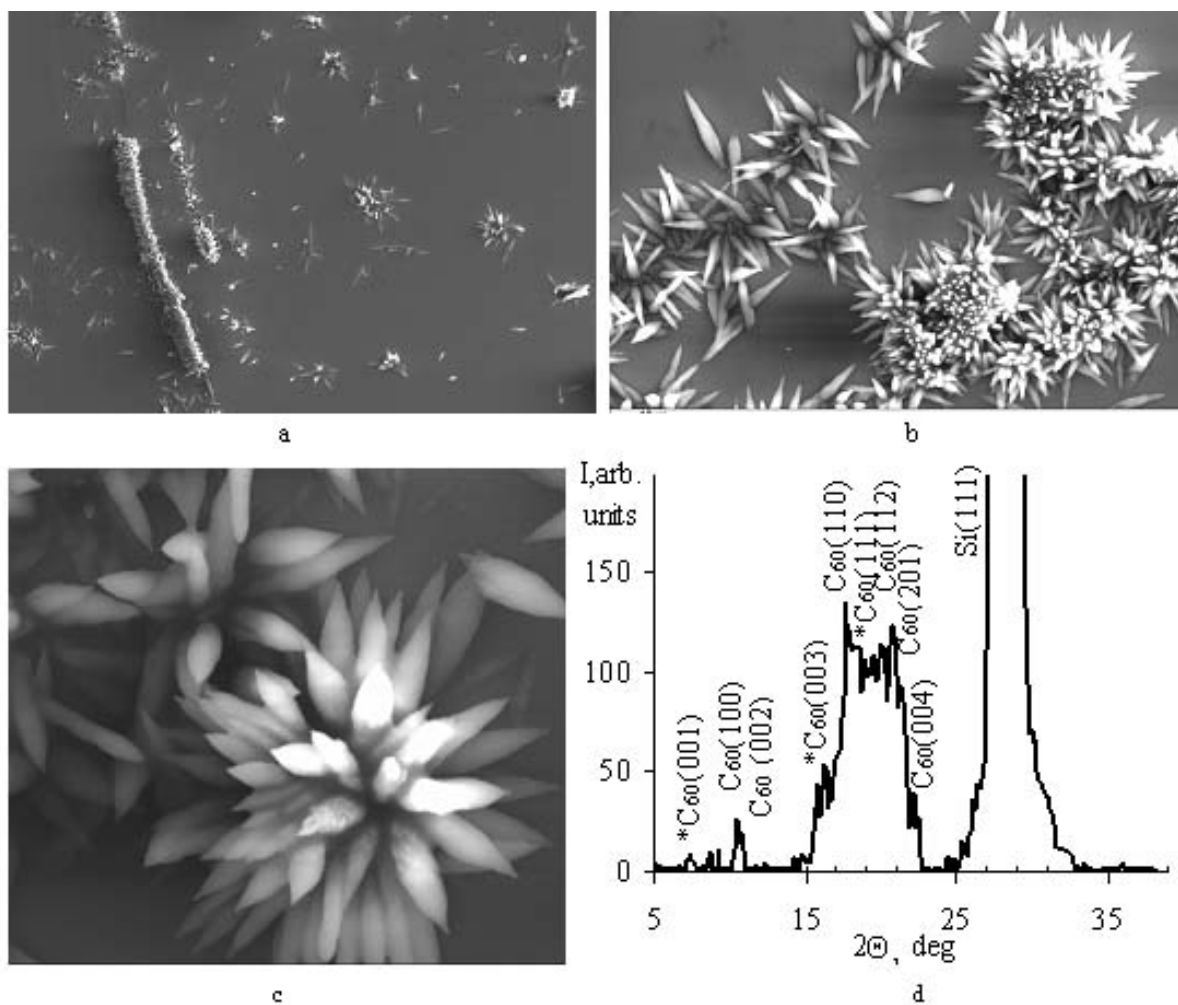


FIG. 4. The structure (a) and X-ray diffraction pattern (b) fullerite films after the in-air storage

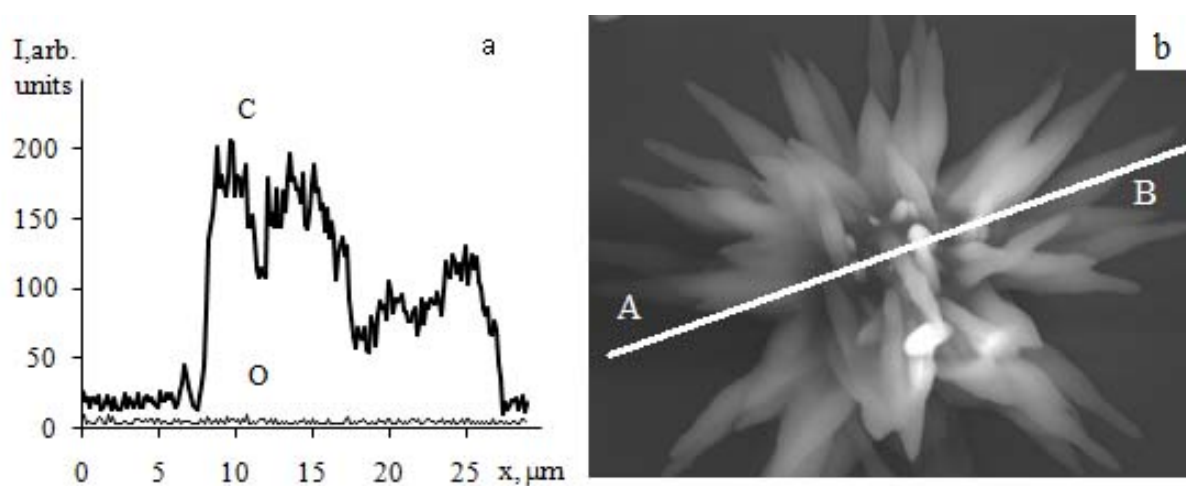


FIG. 5. Distribution of elements (a), obtained by the method of X-ray microanalysis in the electronic beam scanning along the indicated line (shown in panel b) of fullerite films after the in-air storage

4. Conclusions

Thus, as a result of the conducted research, it is established that under condition of aerobic storage over a protracted period (30 months), the spontaneous growth of petal crystals occurs on the surfaces of fullerite films.

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