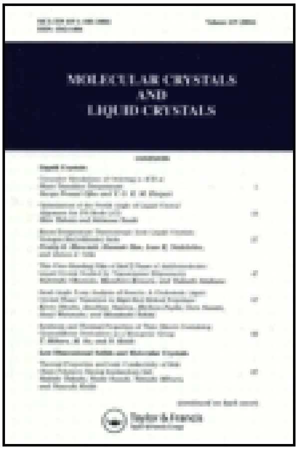

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Structural peculiarities and raman vibrational modes in the C 60 films

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STRUCTURAL PECULIARITIES AND RAMAN VIBRATIONAL MODES IN THE C_{60} FILMS

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The influence of thermal annealing in the air at the temperatures of 393, 453 and 473 K on the morphological and crystalline structure of fullerene C_{60} films was investigated using the X-ray, electron-diffraction and electron-microscopic methods, and also the Raman spectroscopy. It is established that the annealing of C_{60} films leads to the orientation of grains of the fcc phase by plane (110) in parallel to the substrate, the considerable increase of the fcc lattice parameter, the decrease of the hdp phase content and the deformation (change in the form) of C_{60} molecules, which is confirmed by an increase in the intensity of vibrations 1399 and 1425 cm^{-1} and by the appearance of new bands 934, 1592 and 1685 cm^{-1} in the Raman spectra.

Keywords: C_{60} film; thermal annealing; X-ray and electron-diffraction methods; Raman spectroscopy

INTRODUCTION

It is known that at temperatures, which exceed 260 K, the vacuum condensates of the fullerene molecules are crystallized into the polymorphous heterophasic structure, which consists of the face centered cubic (fcc) phase and the layers of the hexagonal densely packed (hdp) structure, appearing due to the high density of packing defects [1–3].

Undoubtedly, that carrying out of the thermal annealing can lead to a change of orientation of the crystallites, content of phases and parameters of their lattices, structural defects and deformation of fullerene C_{60} molecules. However, the carried out earlier measurements did not give response to these questions, since the studies were carried out only by one or two methods, and the data about the influence of thermal annealing on the Raman spectra are not known to us. Therefore, in the present work for studying the change in the structure and form of C_{60} molecules during the thermal annealing the comprehensive investigations of a change in the morphology, crystal structure and form of molecules were carried out using the X-ray, electron-diffraction and electron-microscopic methods, and also the Raman spectroscopy.

The investigated C_{60} films were obtained by the method of the thermal vacuum evaporation of C_{60} powder with a purity not worse than 99.9%. The sublimation temperature from the quartz crucible, heated by tungsten spiral, was equal to 730 K. The films were brought to the NaCl crystals with the chippings (100), mica (0001) and shears of (100) Si, (0001) SiO_2. The thickness of films was tested on the frequency shift of the calibrated quartz vibrator and equal to 100, 400 and 2000 nm.

The thermal annealing of C_{60} films in the air was carried out at the temperatures of 393, 453 and 473 K during from 20 to 300 minutes with the subsequent slow cooling up to 293 K. The morphological and structural peculiarities were studied by use the X-ray, electron-diffraction and electron-microscopic methods, and also on the change in the Raman vibrational spectra of C_{60} films, which passed identical heat treatment. The measurements were carried out at room temperature. During the measurement of Raman spectra as the source of excitation was used argon laser with a wavelength of emission 514.5 nm.

RESULTS AND DISCUSSION

Before the annealing the C_{60} films have the fine-crystalline structure (Fig. 1a) with the starts of separate crystallites (Fig. 1b). The films, applied into NaCl, form the axial texture with the imposition of densely packed planes (111) of fcc phase and (0001) hdp structure across the surface of the substrate (Fig. 2a). The analysis showed, that the following orientational relationship is fulfilled for these planes of fcc and hdp modifications:

$$[110]_{\mathrm{fcc}}\mathrm{II}[100]_{\mathrm{hdp}}.$$

The habitus of the projection of separate grains on the plane of substrate has the pentagonal form, that it is possible to explain by the presence of many twins as the consequence of shifts in the sequence of pilling of hdp phase planes.

The crystallographic analysis of X-ray and electron-diffraction pictures for the fcc structure of fullerite C_{60} gives the following value of lattice

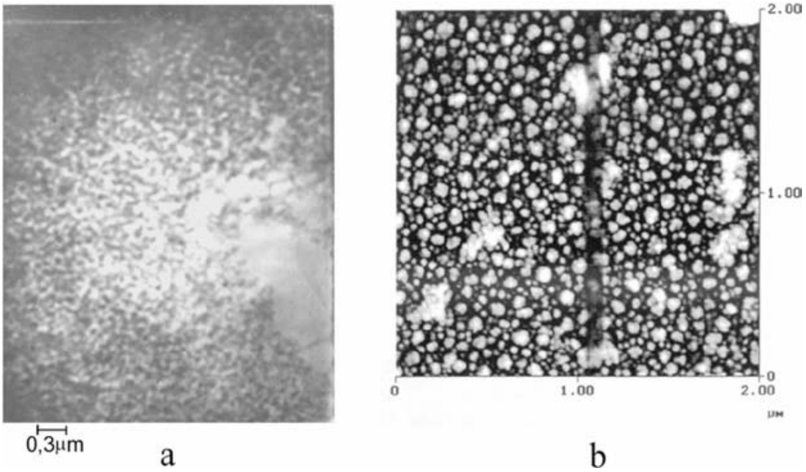

FIGURE 1 Morphology of grains of the C_{60} film: electron-microscopic (a) and atomic-force (b) images (thickness of film is 100 nm).

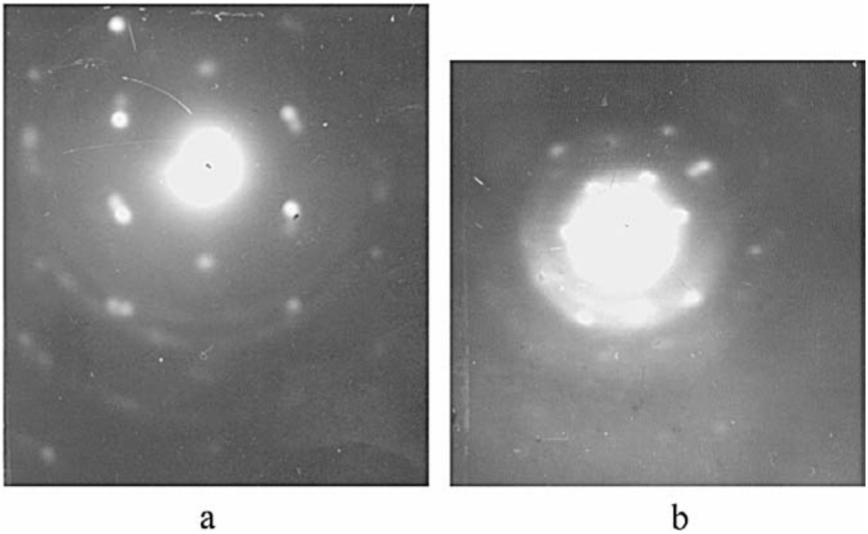

FIGURE 2 The electron diffraction of grains of the C_{60} film: in the initial state of spraying (a) and after the annealing at 473 K during 120 minutes (b) (thickness of film is 100 nm).

parameter a = 1.414 nm, and for the layers of hdp modification we have a = 0.998 nm and c = 1.620 nm.

As a result of annealing at the temperatures of 453 and 473 K the majority of grains are oriented in the plane (110) of fcc phase across the substrate (Fig. 2b), and the hdp structure is not established. Besides the separate large crystallites in the annealed films, the fine dispersed grains, which give Debye scattering, are also remained. The lattice parameter, calculated from the X-ray and electron-diffraction spectra, noticeably rises and as a result of annealing at 473 K during 120 minutes equals to 1.650 nm.

The breathing $A_g(1)$ mode at the frequency of 495.7 cm^{-1} caused by the radial displacement of all atoms, and the $A_g(2)$ mode at the frequency of 1470.8 cm^{-1}, connected with the symmetrical vibrations of pentagons along the surface of molecule, and also eight intramolecular H_g modes are observed in the Raman spectrum of fullerene C_{60} films before the annealing. The frequencies of all modes agree well with those given in the paper [3]. Furthermore, in the Raman spectrum for all films the additional vibration with a frequency of 295.2 cm^{-1} (Fig. 3) is observed, whose intensity substantially changes during the thermal annealing.

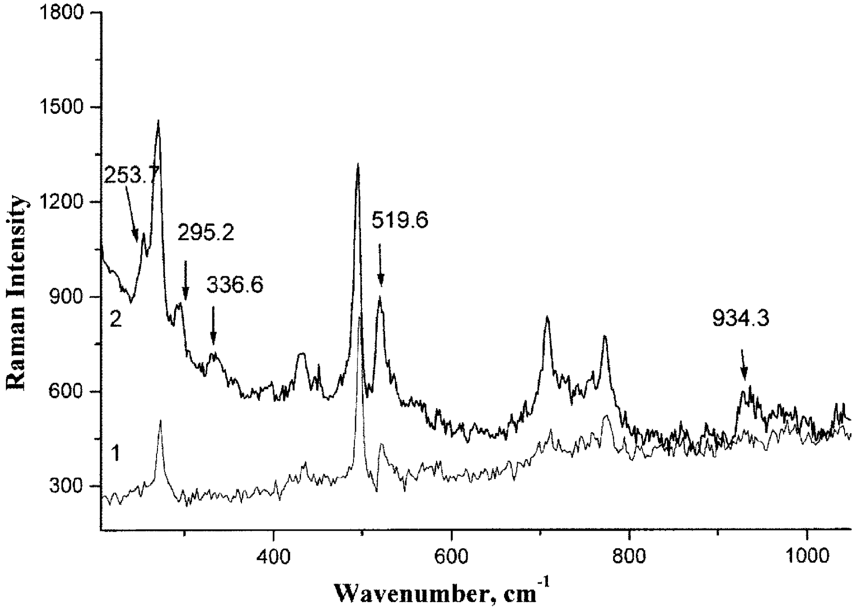

FIGURE 3 Low frequency Raman spectra of the C_{60} films in the initial state of spraying (1) and annealed (2) (Si substrate, thickness is 2000 nm).

The substantial changes in the Raman spectra of C_{60} films are observed already at a temperature of 393 K, which increase with an increase in the temperature of annealing.

The annealing at 453 K during 60 minutes (Fig. 3, curve 2) in the low-frequency region of the spectrum leads to the softening of both the breathing $A_g(1)$ and the intramolecular $H_g(1)$ modes, that undoubtedly caused by the changing of Van-der-Waals interaction, connected with the influence of planar packing defects, whose correlation lead to the origin of hdp modification of the crystal structure. The increase during the annealing of the scattering intensity at the frequency of 295,2 cm^{-1}, connected with the hdp crystalline structure, testifies about the same.

The annealing at 473 K during 120 and 300 minutes leads to increase in the intensity of scattering on the vibrational mode at the frequency 934.3 cm^{-1} and decrease in the intensity of vibration with a frequency of 295.2 cm^{-1}. Taking into account that at the annealing indicated the diffraction pattern of scattering testifies about the stabilization of fcc structure and the disappearance of hdp phase, natural to assume that the noted changes in the Raman spectra are caused by the structural transformations in the crystalline C_{60} films.

With an increase in the temperature of annealing a total increase in the background both in the region of the low and high frequencies of the Raman spectra at the conservation of the fullerene vibrational modes is observed. In this case should be noted the complex behavior of the vibrational $A_g(2)$, $H_g(7)$ and $H_g(8)$ modes in the region of high frequencies (Fig. 4).

First, with an increase in the temperature of annealing the half-width of these lines is noticeably changed. Second, the frequency of the intramolecular $H_g(8)$ mode is displaced to the side of high values, i.e. it approaches to the frequency of $1592\,\text{cm}^{-1}$, which is typical for the fully symmetrical vibrations of graphite. Thirdly, the appearance of additional wide lines of scattering at the frequencies near 1399 and $1685\,\text{cm}^{-1}$ takes place.

This complex behavior of Raman spectra is the result of the imposition of the simultaneous action of several factors, connected with the change of crystal lattice parameters of films and form of C_{60} molecules. A noticeable increase in the lattice parameter of fcc phase at an increase in the temperature of annealing determines the background growth with frequency increase. From other side, it becomes obvious, that already during the heat treatment indicated the C_{60} molecules are deformed, which is accompanied

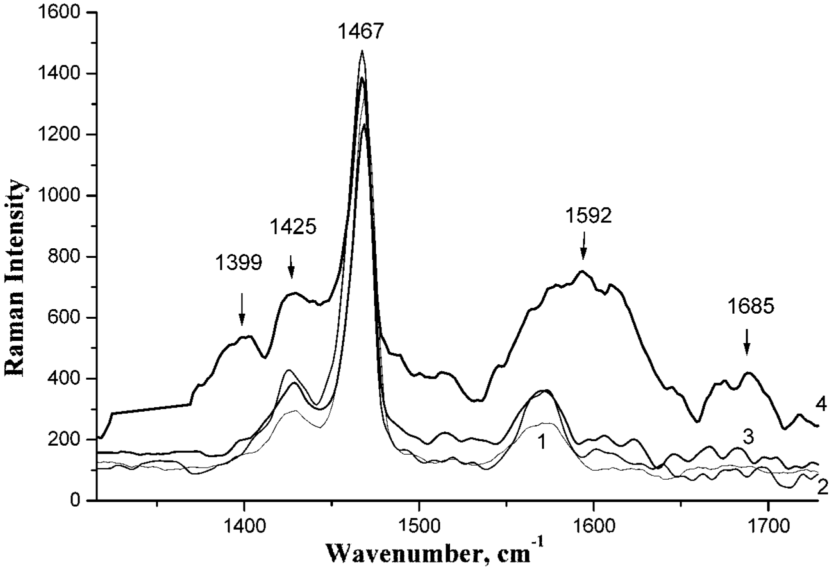

FIGURE 4 High frequency Raman spectra of the C_{60} films in the initial state (1) and annealed at 393 K during 20 minutes (2), at 453 K during 60 minutes (3) and at 473 K during 300 minutes (4).

by the noted transformations in the high frequency region of the Raman spectrum.

Thus, the annealing of C_{60} films in the air in the temperature range of (393–473) K leads to the preferred orientation of the crystallites of fcc phase by plane (110) in parallel to the substrate, the considerable increase of the fcc lattice parameter (from 1.414 to 1.650 nm), the decrease of the hdp phase content, and the deformation (change in the form) of fullerene C_{60} molecules, which leads to a considerable (in 2–3 times) increase in the intensity of vibrations 1399 and 1425 cm^{-1} and the appearance of new bands 934, 1592 and 1685 cm^{-1} in the Raman spectra.

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