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## SURFACE MORPHOLOGY OF THE FILMS OF THE C<sub>60</sub>/C<sub>70</sub> FULLERENE MIXTURE. IDENTIFICATION OF C<sub>60</sub> AND C<sub>70</sub> IN THE C<sub>60</sub>/C<sub>70</sub> FILMS USING ABSORPTION SPECTRA

*Films of the C<sub>60</sub>/C<sub>70</sub> mixture are deposited onto various substrates in a vacuum of 6.5 mPa using the thermal sublimation method. The surface morphology of 195-nm C<sub>60</sub>/C<sub>70</sub> films is studied. It is found that polycrystalline and quasi-amorphous C<sub>60</sub>/C<sub>70</sub> films are formed on silica and copper substrates, respectively. The nature of the C<sub>60</sub> and C<sub>70</sub> absorption bands has been discussed in detail by analyzing the literature and our data. The absorption spectra of the C<sub>60</sub> and C<sub>70</sub> films and the C<sub>60</sub>/C<sub>70</sub> mixture films are described as the sum of Gaussian functions. The absorption bands of C<sub>60</sub> (at 2.474, 3.440, and 3.640 eV) and C<sub>70</sub> (at 2.594, 2.804, 3.018, and 3.252 eV) can be used to identify those substances in fullerene mixtures. C<sub>60</sub> is found to be the dominant component in the C<sub>60</sub>/C<sub>70</sub> films.*

*Keywords:* thin film, surface morphology, absorption spectra, fitting, Gaussians, C<sub>60</sub>/C<sub>70</sub> mixture.

### 1. Introduction

The C<sub>60</sub> and C<sub>70</sub> fullerenes were discovered in 1985 [1]. A molecular quasi-spherical cluster C<sub>60</sub> is formed by 12 pentagonal and 20 hexagonal faces with 60 carbon atoms at their vertices. Such a cluster is described by the point symmetry group  $I_h$ . A molecular cluster C<sub>70</sub> has a quasi-ellipsoidal shape owing to additional 5 hexagonal faces along the equatorial line, and it is described by the point symmetry group  $D_{5h}$  [2].

C<sub>60</sub> and C<sub>70</sub> materials are widely used as electron acceptors in organic solar cells [3]. C<sub>60</sub> was applied in solar cells [4], photovoltaic devices [5], photocatalysts [6], phototherapy [7], and biosensors [8]. C<sub>70</sub> is suitable for replacing C<sub>60</sub> in organic solar cells. For instance, the light conversion efficiency  $\eta$  in bulk heterojunctions was 2.87% in the C<sub>70</sub>/zinc phthalocyanine (ZnPc) heterojunction and 2.27% in

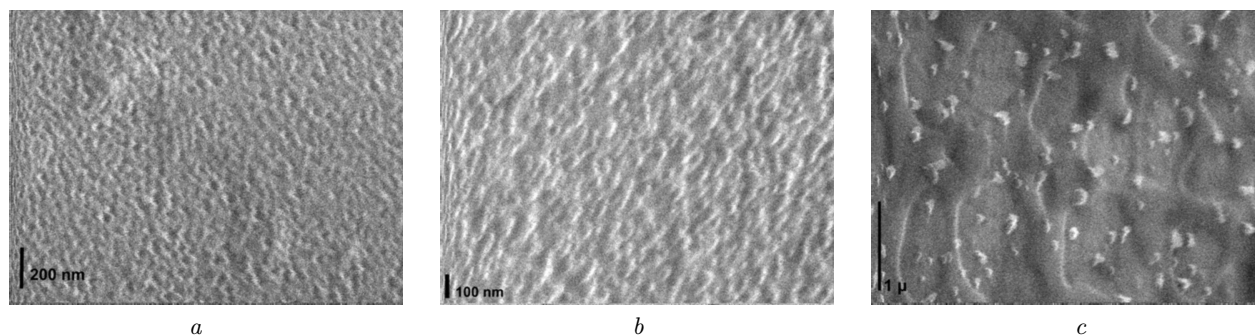
the C<sub>60</sub>/ZnPc one. The larger value of  $\eta$  is a result of the stronger light absorption by C<sub>70</sub> in a spectral interval of 1.771–2.480 nm [9]. The optical absorption spectra of “pure” C<sub>60</sub> (99.86% purity) and C<sub>70</sub> (>99% purity) were registered in *n*-hexane at room temperature [10].

In work [10], C<sub>60</sub> and C<sub>70</sub> were obtained using the method of Krättschmer *et al.* [11]. Then they were extracted from the benzene solution of initial graphite soot and purified using the column chromatography method.

The optical absorption spectra of C<sub>60</sub> in *n*-hexane solutions and the nature of their bands were studied in work [12]. The optical absorption spectra of the C<sub>60</sub> and C<sub>70</sub> films were studied in works [11, 13, 14] and [15], respectively. It was found that the absorption bands of the C<sub>60</sub> and C<sub>70</sub> films are shifted to the red with respect to the corresponding bands in the spectra of their solutions, which is a result of the intermolecular interaction in the solid state.

A review of the most important theoretical and experimental papers aimed at elucidating the properties of the lowest excited states in C<sub>60</sub> and C<sub>70</sub> was made in work [16]. The diagrams of the energy levels of the C<sub>60</sub> and C<sub>70</sub> molecules were given in works [2, 14, 17–21].

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**Fig. 1.** SEM micrographs of 195-nm  $C_{60}/C_{70}$  films deposited in vacuum on silica substrates with thin carbon (a) and ITO (b) layers, and on a copper substrate (c)

According to the mass spectrometry data [10], when the fullerenes are synthesized, molecules with various numbers of carbon atoms are formed. They are described by the general formula  $C_{2n}$ , where the natural number  $n$  varies from 26 to 35. The most stable components of this mixture are the  $C_{60}$  and  $C_{70}$  molecules. Therefore, the study of the absorption spectra of the solutions and films of pure  $C_{60}$  and  $C_{70}$  substances is a challenging task for their identification in solid mixtures of synthesized fullerenes.

In this work, the surface morphology of the  $C_{60}/C_{70}$  films and the nature of the absorption bands of  $C_{60}$  and  $C_{70}$  in the molecular and solid states are studied in order to identify those substances by their bands in the absorption spectra of the films of  $C_{60}/C_{70}$  mixtures.

## 2. Specimen Preparation and Experimental Technique

In our research, we used a mixture of fullerenes (MER Corporation) with the following composition: 76%  $C_{60}$ , 22%  $C_{70}$ , and 2% higher-order fullerenes. Hereafter, this mixture will be denoted by  $C_{60}/C_{70}$  according to its main components.

To study their optical absorption properties, thin  $C_{60}/C_{70}$  films with various thicknesses  $d$  within an interval of 25–195 nm were deposited onto silica substrates in a vacuum of 6.5 mPa using the thermal sublimation method. The initial  $C_{60}/C_{70}$  mixture was sublimated from a ceramic crucible heated up by passing an electric current through a nichrome spiral. During the sputtering process, the temperature of the ceramic crucible varied from 673 to 723 K; it was measured with the help of a chromel-alumel thermocouple.

The start and final moments of the film deposition were registered using a thickness gauge MSV-1841. The film thickness was measured by means of an interference thickness gauge MII-4.

The absorption spectra of thin  $C_{60}/C_{70}$  films within an interval of 1.305–4.133 eV were registered at room temperature using a Perkin Elmer Lambda 25 UV-Vis spectrophotometer with a spectral slit width of 1 nm. The absorption measurement error did not exceed 2%.

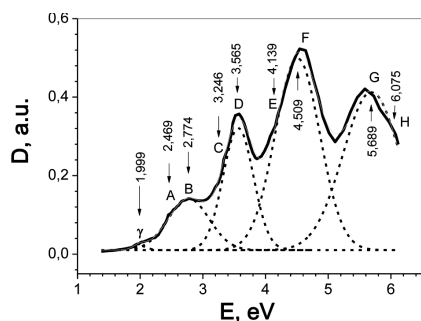
The surface morphology of  $C_{60}/C_{70}$  films deposited onto silica substrates with thin carbon or indium tin oxide (ITO) layers and onto copper substrates was studied with the help of a JSM-35 JEOL scanning electron microscope.

## 3. Results and Their Discussion

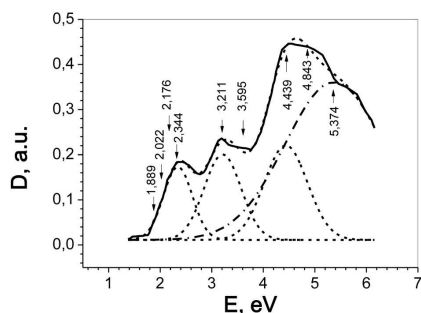
### 3.1. Surface morphology of $C_{60}/C_{70}$ films

The surface morphology of solid 195-nm  $C_{60}/C_{70}$  films deposited in a vacuum of 6.5 mPa is shown in Fig. 1. Needle-like and round crystallites of various sizes are clearly seen in Figs. 1, a and 1, b. They were formed due to the van der Waals interaction between the  $C_{60}$  and  $C_{70}$  molecules. The carbon and ITO layers affect the orientation of needle-like crystallites. A higher orientation ability of the ITO layer (Fig. 1, b) is evident.

The mobility of the sublimated  $C_{60}$  and  $C_{70}$  molecules is restricted by their strong interaction with Cu atoms. In this case, a quasi-amorphous  $C_{60}/C_{70}$  layer first appears on the copper substrate surface. The fullerene molecules located on the surface of this layer interact less strongly with Cu atoms and, due to the van der Waals interaction, be-



**Fig. 2.** Absorption spectrum of the 20-nm  $C_{60}$  film on a silica substrate at room temperature (solid curve) (taken from [9]). Fitting of this spectrum by five Gaussians (dashed curves)



**Fig. 3.** Absorption spectrum of the 20-nm  $C_{70}$  film on a silica substrate at room temperature (solid curve) (taken from [9]). Fitting of this spectrum by four Gaussians (dashed curves)

come the formation centers of rounded crystallites at various places of the quasi-amorphous layer surface (Fig. 1, c).

The size of crystallites on all three substrates varies from 50 to 200 nm.

The SEM micrographs (Fig. 1) demonstrate the influence of the interaction between the fullerenes and the substrates on the structure of  $C_{60}/C_{70}$  films.

### 3.2. Optical absorption spectra of $C_{60}$ , $C_{70}$ , and $C_{60}/C_{70}$ films

In this work, the absorption spectra of the  $C_{60}$  (Fig. 2) and  $C_{70}$  (Fig. 3) films were approximated by the sums of Gaussian functions using the Origin 8.5 software. The standard deviation was  $6.2 \times 10^{-5}$ , and the correlation coefficient 0.99682.

The energies of the transition in the spectra of the imaginary component  $\varepsilon_2$  of the dielectric function of  $C_{60}$  hexane solutions ( $\varepsilon_2$ -spectra), as well as their assignments, are quoted in Table 1 (columns 2 and 3, respectively). The transition  $h_u \rightarrow t_{1u}$  (band  $\gamma$ ) is forbidden, because it occurs between antisymmetric

electronic states. This transition becomes allowed because of its interaction with the corresponding symmetric molecular vibrations (the Herzberg–Teller or Jahn–Teller coupling) [22]. Allowed transitions occur between electronic states with different symmetries. The strengths of their oscillators are different. The degenerate electronic levels  $h_u$  and  $(h_g, g_g)$  correspond to the HOMO and HOMO – 1 molecular orbitals, respectively.

The transition energies in the absorption spectra of  $C_{60}$  films are quoted in Table 1 (column 6) and indicated in Fig. 2. As a result of the molecular interaction in the  $C_{60}$  films, the molecular levels of excited states are split into narrow energy zones. When fitting the absorption spectrum profile of  $C_{60}$  films, the Gaussian functions for zones  $\gamma$ , B, D, F, and G were determined. Zones A, C, and E look like shoulders (sh) on the low-energy side of bands B, D, and F, respectively (Fig. 2). Bands C and H were observed in the absorption spectra of hexane solutions and  $C_{60}$  films, but they were absent in the  $\varepsilon_2$ -spectra of the  $C_{60}$  molecule (see Table 1, columns 2 and 3).

The transition energies in the absorption spectra of the films of  $C_{70}$  and its hexane solution are quoted in Table 2. Column 4 of this table contains data for the spectrum of the 20-nm  $C_{70}$  film (Fig. 3). They are consistent with the data of work [15] (see Table 2, column 3). The absorption peaks for  $C_{70}$  films are red-shifted with respect to the corresponding peaks for the  $C_{70}$  hexane solution [10, 23] (see Table 2, columns 1 and 2).

The energy structure of the  $C_{70}$  molecule was calculated *ab initio* in work [24] in the framework of the Hartree–Fock method. According to the results of those calculations, the energy level diagram of the  $C_{70}$  molecule was plotted in work [25]. We have analyzed those data and changed the level symmetry for some HOMO and LUMO molecular orbitals given in work [25], after comparing them with the relevant data from work [24]. So the symmetries of the HOMO – 5, LUMO, and LUMO + 1 levels were changed to  $a'_1$ ,  $e''_1$ , and  $a''_1$ , respectively. According to work [24], the LUMO + 4 and LUMO + 5 levels have the  $e'_2$  and  $a''_2$  symmetries, respectively, and they were used to explain the possible origin of transitions with energies  $E \geq 3.605$  eV. The transitions in the  $C_{70}$  molecule are quoted in column 5 of Table 2.

The difference between the transition energies of 2.022 and 1.889 eV (Table 2, column 4) equals

**Table 1. Transition energies, oscillator strengths (in parentheses), and assignments of C<sub>60</sub> absorption bands at room temperature**

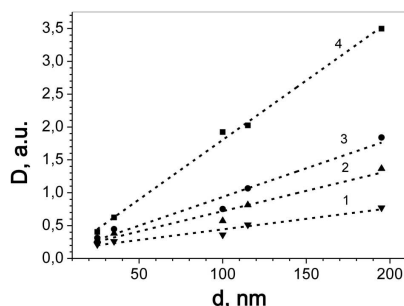
Band code	$\epsilon_2$ -spectra of C <sub>60</sub> -hexane solution [14]		Absorption spectra C <sub>60</sub> -hexane solution [12]		Absorption spectrum of 20-nm C <sub>60</sub> film (this work)
	$E$ , eV	Assignment	$E$ , eV	Assignment	$E$ , eV
1	2	3	4	5	6
$\gamma$	1.995 (0.001)	$h_u \rightarrow t_{1u}$	1.999	$A_g \rightarrow 1T_{1g}$	1.999
A		$h_u \rightarrow t_{1g}$	3.037	$A_g \rightarrow 1T_{1u}$	2.469 (sh)
B	3.280 (0,001)	$h_u \rightarrow t_{1g}$	3.289	$A_g \rightarrow 2T_{1u}$	2.774
C			3.775	$A_g \rightarrow 3T_{1u}$	3.246 (sh)
D <sub>1</sub>	3.580 (0.080)	$h_g, g_g \rightarrow t_{1u}$	4.065	$A_g \rightarrow 4T_{1u}$	3.565
D <sub>2</sub>	3.732 (0,090)	$h_g, g_g \rightarrow t_{1u}$	4.350	$A_g \rightarrow 5T_{1u}$	
E	4.210 (0,040)	$h_u \rightarrow h_g$	4.832	$A_g \rightarrow 6T_{1u}$	4.139 (sh)
F	4.600 (0.490)	$h_u \rightarrow h_g$	5.452	$A_g \rightarrow 7T_{1u}$	4.509
G <sub>1</sub>	5.437 (0.019)	$h_g, g_g \rightarrow t_{2u}$	5.876	$A_g \rightarrow 8T_{1u}$	5.689
G <sub>2</sub>	5.730 (0.330)	$h_g, g_g \rightarrow t_{2u}$			
H			6.358	$A_g \rightarrow 9T_{1u}$	6.075 (sh)

Note: abbreviation sh stands for shoulder.

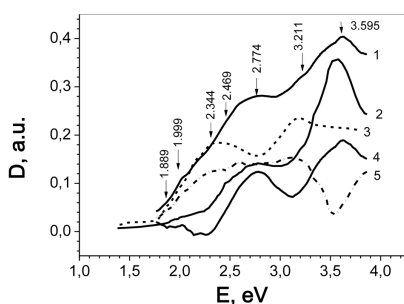
**Table 2. Transition energies, relative intensities (in parentheses), and assignments of C<sub>70</sub> absorption bands at room temperature**

Absorption spectra of C <sub>70</sub>				
Transition energies $E$ , eV				Assignment [24, 25]
In hexane		Film		
[10]	[23]	[15]	This work	
1	2	3	4	5
	1.864 (sh)	1.890	1.889 (sh)	$e''_1 \rightarrow e''_1$ or $a''_2 \rightarrow a''_1$
1.946 (sh)	1.992 (sh)			
1.986 (sh)	1.999 (sh)			
2.033 (sh)		2.026	2.022 (sh)	$e''_1 \rightarrow e''_1 + E'_1$ or $a''_2 \rightarrow a''_1 + E'_1$
2.066 (sh)	2.066 (sh)			
2.087 (sh)		2.183	2.176 (sh)	$a'_2 \rightarrow e''_1$
2.279 (sh)	2.254 (sh)	2.353	2.344	$e''_2 \rightarrow a''_1$
2.644 (sh)	2.649 (sh)	2.485		$e'_1 \rightarrow a''_1$ or $a''_2 \rightarrow a'_1$
3.280 (mw)	3.280 (mw)	3.204	3.211	$e'_2 \rightarrow e'_1$ or $a'_2 \rightarrow e'_1$ , or $a'_1 \rightarrow a''_1$
3.454 (mw)	3.444 (mw)	3.416		$e'_1 \rightarrow a'_1$
3.745 (mw)	3.745 (mw)	3.605	3.595 (sh)	$e'_1 \rightarrow e'_2$
3.961 (w)		4.495	4.439	$a'_2 \rightarrow a''_2$
5.767 (s)	5.794 (s)	5.688	5.374	$a'_1 \rightarrow a''_2$

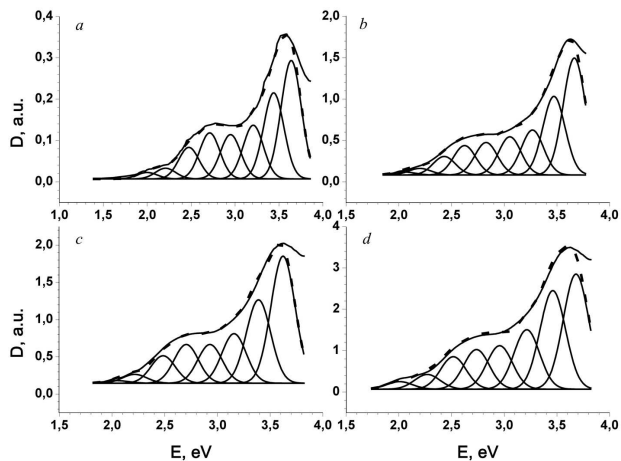
Note: abbreviation mw stands for mean weak, w for weak, s for strong, and sh for shoulder.



**Fig. 4.** Linear fitting (dashed lines) of the optical density function  $D(d)$  of  $C_{60}/C_{70}$  films measured at incident photon energies of 2.412 (1), 2.800 (2), 3.196 (3), and 3.625 eV (4)

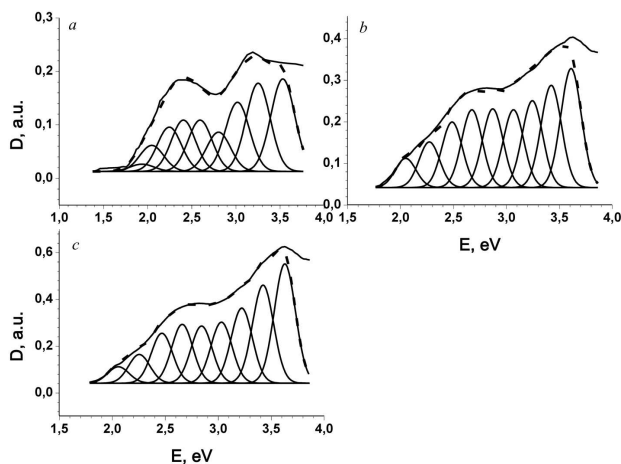


**Fig. 5.** Absorption spectra of films on silica substrates: (1)  $C_{60}/C_{70}$  mixture,  $d = 25$  nm; (2)  $C_{60}$ ,  $d = 20$  nm; (3)  $C_{70}$ ,  $d = 20$  nm; (4) difference between curves 1 and 3; (5) difference between curves 1 and 2



**Fig. 6.** Fitting of the film absorption spectra by the sums of the Gaussians with the same width (dashed curves):  $C_{60}$ ,  $d = 20$  nm (a);  $C_{60}/C_{70}$ ,  $d = 100$  nm (b);  $C_{60}/C_{70}$ ,  $d = 115$  nm (c); and  $C_{60}/C_{70}$ ,  $d = 195$  nm (d)

0.133 eV  $\approx$  1073  $cm^{-1}$ . In work [15], the corresponding difference was found to equal 0.136 eV  $\approx$  1097  $cm^{-1}$  (Table 2, column 3). By magnitude, those



**Fig. 7.** Fitting of the film absorption spectra by the sums of the Gaussians with the same width (dashed curves):  $C_{70}$ ,  $d = 20$  nm (a);  $C_{60}/C_{70}$ ,  $d = 35$  nm (b); and  $C_{60}/C_{70}$ ,  $d = 35$  nm (c)

values are close to the IR frequency of  $C_{70}$   $E'_1 = 1087$   $cm^{-1}$  [26]. One may assume that the absorption bands at 2.026 and 2.022 eV are a result of the interaction of the excited states  $e''_1$  and  $a''_1$  with the 1087- $cm^{-1}$  vibration (the Herzberg-Teller or Jahn-Teller coupling as in the  $C_{60}$  molecule [22]). Those bands can be considered as the transitions  $e''_1 \rightarrow e''_1 + E'_1$  and  $a''_2 \rightarrow a''_1 + E'_1$ .

According to the Bouguer-Lambert law, we evaluated the effective absorption coefficients  $\alpha(E)$  of the  $C_{60}/C_{70}$  films as the slopes of the plots  $D(d)$  (Fig. 4). The values obtained for  $\alpha(E)$  are  $3.22 \times 10^4$   $cm^{-1}$  for line 1,  $6.16 \times 10^4$   $cm^{-1}$  for line 2,  $8.71 \times 10^4$   $cm^{-1}$  for line 3, and  $1.82 \times 10^5$   $cm^{-1}$  for line 4. The relative measurement error of  $\alpha(E)$  did not exceed 12%. Smaller relative measurement errors were obtained for larger  $\alpha(E)$ . The smallest error was for an incident photon energy of 3.625 eV (line 4) and amounted to 2%. The  $\alpha(E)$ -values calculated from the absorption spectra of the  $C_{60}$  and  $C_{70}$  films with  $d = 20$  nm for photon energies of 2.412, 2.800, 3.196, and 3.625 eV are as follows:  $3.8 \times 10^4$ ,  $6.7 \times 10^4$ ,  $8.1 \times 10^4$ , and  $1.7 \times 10^5$   $cm^{-1}$ , respectively, for the  $C_{60}$  films; and  $8.5 \times 10^4$ ,  $7.2 \times 10^4$ ,  $1.1 \times 10^5$ , and  $1.0 \times 10^5$   $cm^{-1}$ , respectively, for the  $C_{70}$  ones. A comparison of those data shows that the above-presented values of  $\alpha(E)$  for the  $C_{60}/C_{70}$  films better correlate with the  $\alpha(E)$ -values calculated for the  $C_{60}$  films at the corresponding energies of incident photon. This fact means that  $C_{60}$  is the main component in the  $C_{60}/C_{70}$  films.

In an energy interval of 1.38–3.31 eV, the absorption of the  $C_{70}$  film is stronger than that of the  $C_{60}$  film (Fig. 5, curves 3 and 2, respectively). In Fig. 5, the numbers near the arrows mean the transition energies for the  $C_{60}$  and  $C_{70}$  films, which were taken from Table 1 (column 5) and Table 2 (column 4). The  $C_{60}$  contribution (curve 4) to the  $C_{60}/C_{70}$  absorption was calculated by subtracting the  $C_{70}$  spectrum (curve 3) from the mixture one (curve 1). Absorption spectrum 4 correlates with spectrum 2 of the  $C_{60}$  film. Absorption spectrum 5 characterizes the  $C_{70}$  contribution to the  $C_{60}/C_{70}$  absorption. This spectrum was obtained by subtracting spectrum 2 from spectrum 1, and it correlates with  $C_{70}$  spectrum 3 in an interval of 1.8–3.6 eV. At the same time, the anti-correlation between the absorption spectra for the  $C_{60}$  and  $C_{70}$  films (curves 2 and 3, respectively) was observed. Absorption spectra 4 and 5 also anti-correlate. Hence, from the above analysis of the absorption spectra shown in Fig. 5, it follows that both  $C_{60}$  and  $C_{70}$  enter the composition of the  $C_{60}/C_{70}$  film.

### 3.3. Identification of $C_{60}$ and $C_{70}$ in $C_{60}/C_{70}$ films by absorption spectra

In an interval of 1.38–6.0 eV, the absorption spectra of the  $C_{60}$  (Fig. 2) and  $C_{70}$  (Fig. 3) films consist of wide structural bands. In Figs. 6 and 7, the structural absorption bands of the  $C_{60}$ ,  $C_{70}$ , and  $C_{60}/C_{70}$  films are resolved as the sums of the Gaussian functions of the same width. It was done in order to determine the transition energies more accurately and to compare them within an interval of 1.38–3.80 eV. The fitting by Gaussians of the same width allows the structure of the absorption spectra of the  $C_{60}$ ,  $C_{70}$ , and  $C_{60}/C_{70}$  films to be resolved more accurately and provides an opportunity to qualitatively reveal the composition dynamics of the  $C_{60}/C_{70}$  films with various thicknesses during the thermal sputtering of this mixture.

The absorption spectra of the  $C_{60}$ ,  $C_{70}$ , and  $C_{60}/C_{70}$  films are grouped according to the similarity of their profiles. The absorption spectra of the  $C_{60}$  ( $d = 20$  nm) and  $C_{60}/C_{70}$  ( $d = 100, 115,$  and  $195$  nm) films together with their fitting by the sums of Gaussian functions of the same width are shown in Fig. 6. Analogous fittings of the absorption spectra of the  $C_{70}$  ( $d = 20$  nm) and  $C_{60}/C_{70}$  ( $d = 25$  and  $35$  nm) films are depicted in Fig. 7 (panels *a*, *b*, and

*c*, respectively). The relative intensity of each Gaussian was determined as the ratio  $A/A_0$  between the area  $A$  under this Gaussian component and the total area  $A_0$  under the absorption spectrum of the film, the latter being equal to the sum of the areas under all Gaussian components that form the spectrum.

The values of the energies and relative intensities of electronic transitions in the absorption spectra of the  $C_{60}$  and  $C_{60}/C_{70}$  films, which were determined from Fig. 6, are given in Table 3, and their counterparts determined for the  $C_{70}$  and  $C_{60}/C_{70}$  films from Fig. 7 are quoted in Table 4. The numbers in the second column (Band code) of those tables are the numbers of Gaussian components ( $C_{60}$  or  $C_{70}$ ) in the absorption spectra of the  $C_{60}/C_{70}$  films with  $d = 25, 35, 100, 115,$  and  $195$  nm.

#### 3.3.1. $C_{60}$ contributions to the absorption spectra of $C_{60}/C_{70}$ mixture films

The weak band at 2.007 eV, which was observed only in the absorption spectrum of the 195-nm  $C_{60}/C_{70}$  film (Table 3, row 1), was identified by us as band 1\_  $C_{60}$  ( $\gamma$ -band) at 1.999 eV (Table 1, row 1).

In the absorption spectra of the  $C_{60}/C_{70}$  films with  $d = 100, 115,$  and  $195$  nm, there appears band 2\_  $C_{60}$  at 2.209 eV (Table 3, row 3), which is absent in the absorption spectra of thin  $C_{60}/C_{70}$  films with  $d = 25$  and  $35$  nm.

Band 3\_  $C_{60}$  at 2.474 eV, which was identified as band A (Table 1), was observed in the absorption spectra of the  $C_{60}/C_{70}$  films of all thicknesses (Table 3, row 4; Table 4, row 5). Its relative intensity is minimum in the absorption spectrum of the 100-nm  $C_{60}/C_{70}$  film.

In the absorption spectra of the  $C_{60}/C_{70}$  films with  $d = 115$  and  $195$  nm, bands 4\_  $C_{60}$  and 5\_  $C_{60}$  are observed; the latter at 2.712 eV (band B, Table 1) for the film thickness  $d = 115$  nm and at 2.949 eV for  $d = 195$  nm. The relative intensities of those bands change insignificantly with the growth of the  $C_{60}/C_{70}$  film thickness (Table 3, rows 6 and 8).

Band 6\_  $C_{60}$  at 3.208 eV (band C, Table 1) is observed in the absorption spectra of the  $C_{60}/C_{70}$  films with  $d = 115$  and  $195$  nm. The relative intensity of this band increases as the thickness  $d$  of the  $C_{60}/C_{70}$  film grows (Table 3, row 10).

Bands 7\_  $C_{60}$  at 3.440 eV (Table 1, band D<sub>1</sub>) and 8\_  $C_{60}$  at 3.640 eV (Table 1, band D<sub>2</sub>) are observed in the absorption spectra of all  $C_{60}/C_{70}$  films (Table 3,

**Table 3. Energies  $E$  and relative intensities  $A/A_0$  of electronic transitions in 20-nm  $C_{60}$  films, and in 100-, 115-, and 195-nm  $C_{60}/C_{70}$  films**

No.	Band code	$C_{60}$ , 20 nm $A_0 = 0.27799$ a.u.		$C_{60}/C_{70}$ , 100 nm $A_0 = 1.17812$ a.u.		$C_{60}/C_{70}$ , 115 nm $A_0 = 1.45257$ a.u.		$C_{60}/C_{70}$ , 195 nm $A_0 = 3.00815$ a.u.	
		$E$ , eV	$A/A_0$	$E$ , eV	$A/A_0$	$E$ , eV	$A/A_0$	$E$ , eV	$A/A_0$
1	<b>1_</b> $C_{60}$	1.999	0.016					2.007	0,018
2	2_		2.050	0.008	2.048	0.006			
3	<b>2_</b> $C_{60}$	2.209	0.027	2.200	0.018	2.214	0.024	2.270	0.036
4	<b>3_</b> $C_{60}$	2.474	0.079	2.431	0.050	2.484	0.073	2.517	0.079
5	5_		2.624	0.080					
6	<b>4_</b> $C_{60}$	2.712	0.116			2.704	0.103	2.737	0.096
7	6_		2.828	0.088					
8	<b>5_</b> $C_{60}$	2.949	0.112			2.929	0.103	2.957	0.106
9	7_		3.053	0.104					
10	<b>6_</b> $C_{60}$	3.208	0.135			3.157	0.131	3.214	0.145
11	8_		3.268	0.122					
12	<b>7_</b> $C_{60}$	3.440	0.216	3.472	0.213	3.389	0.222	3.461	0.240
13	<b>8_</b> $C_{60}$	3.640	0.298	3.665	0.317	3.622	0.338	3.681	0.280

**Table 4. Energies  $E$  and relative intensities  $A/A_0$  of electronic transitions in 20-nm  $C_{70}$  films, and in 25- and 35-nm  $C_{60}/C_{70}$  films**

No.	Band code	$C_{70}$ , 20 nm $A_0 = 0.29865$ a.u.		$C_{60}/C_{70}$ , 25 nm $A_0 = 0.39903$ a.u.		$C_{60}/C_{70}$ , 35 nm $A_0 = 0.60292$ a.u.	
		$E$ , eV	$A/A_0$	$E$ , eV	$A/A_0$	$E$ , eV	$A/A_0$
1	1_	1.936	0.016				
2	2_	2.047	0.055	2.049	0.043	2.057	0.029
3	3_	2.245	0.094	2.272	0.067	2.254	0.051
4	4_	2.405	0.110				
5	<b>3_</b> $C_{60}$			2.487	0.096	2.468	0.088
6	5_	2.594	0.110	2.674	0.114	2.660	0.104
7	6_	2.804	0.083	2.871	0.115	2.848	0.101
8	7_	3.018	0.147	3.067	0.114	3.030	0.108
9	8_	3.252	0.188	3.245	0.127	3.222	0.133
10	<b>7_</b> $C_{60}$			3.423	0.150	3.423	0.174
11	9_	3.531	0.197				
12	<b>8_</b> $C_{60}$			3.610	0.174	3.629	0.211

rows 12 and 13; Table 4, rows 10 and 12). Their relative intensities increase with the increasing thickness of the  $C_{60}/C_{70}$  films.

The data presented above confirm the presence of the  $C_{60}$  component in the  $C_{60}/C_{70}$  films with  $d = 25$ , 35, 100, 115, and 195 nm. The calculated average values of the transition energies and relative intensities (in parentheses) of bands  $3_$  $C_{60}$ ,  $7_$  $C_{60}$ , and  $8_$  $C_{60}$  in the spectra of the  $C_{60}/C_{70}$  films with all

thicknesses are 2.477 eV (0.077), 2.434 eV (0.200), and 3.641 eV (0.264), respectively, and agree well with the following data obtained for the 20-nm  $C_{60}$  films: 2.474 eV (0.079), 3.440 eV (0.216), and 3.640 eV (0.298), respectively (Tables 3 and 4). Therefore, the bands at 2.474, 3.440, and 3.640 eV can be used to identify  $C_{60}$  in the fullerene mixture films by analyzing their absorption spectra. The relative variations of the energy of the  $C_{60}$  peaks at 2.474, 3.440, and

3.640 eV in the spectra of the C<sub>60</sub>/C<sub>70</sub> films with  $d = 25, 35, 100, 115,$  and 195 nm are as follows: 0.5%, -0.2%, -1.7%, 0.4%, and 1.7%, respectively, for the peak at 2.474 eV; -0.5%, -0.5%, 0.9%, -1.5%, and 0.6%, respectively, for the peak at 3.440 eV; and -0.8%, -0.3%, 0.7%, -0.5%, and 1.1%, respectively, for the peak at 3.640 eV.

### 3.3.2. C<sub>70</sub> contributions to absorption spectra of C<sub>60</sub>/C<sub>70</sub> mixture films

Weak band 1\_C<sub>70</sub> at 1.936 eV was not observed in the absorption spectra of the C<sub>60</sub>/C<sub>70</sub> films (Table 4, row 1). By its position, this band is close to 1.889 eV, the energy of the transition  $e''_1 \rightarrow e'_1$  or  $a''_2 \rightarrow a'_1$  (Table 2).

Weak band 2\_C<sub>70</sub> at 2.047 eV was observed in the absorption spectra of the C<sub>60</sub>/C<sub>70</sub> films with  $d = 25, 35, 100,$  and 115 nm. The relative intensity of this band decreases as the thickness of the C<sub>60</sub>/C<sub>70</sub> films grows and is very low in the absorption spectra of the 100- and 115-nm C<sub>60</sub>/C<sub>70</sub> films (Table 4, row 2; Table 3, row 2).

The absorption spectra of the C<sub>60</sub>/C<sub>70</sub> films with  $d = 25$  and 35 nm contain band 3\_C<sub>70</sub> at 2.245 eV. The relative intensity of this band decreases, as the thickness of the C<sub>60</sub>/C<sub>70</sub> films grows (Table 4, row 3). The maximum of this band is located in the middle between the C<sub>70</sub> bands at 2.176 eV (the  $a'_2 \rightarrow e''_1$  transition) and 2.344 eV (the  $e''_2 \rightarrow a''_1$  transition) (Table 2).

In the absorption spectra of the C<sub>60</sub>/C<sub>70</sub> films, band 4\_C<sub>70</sub> at 2.405 eV is absent (Table 4, row 4).

Band 5\_C<sub>70</sub> at 2.594 eV was observed in the absorption spectra of the C<sub>60</sub>/C<sub>70</sub> films with  $d = 25, 35,$  and 100 nm. The relative intensity of this band decreases with the growth of the C<sub>60</sub>/C<sub>70</sub> film thickness (Table 4, row 6; Table 3, row 5). According to the position of its peak, this band is close to the C<sub>70</sub> band at 2.485 eV (the transition  $e'_2 \rightarrow e'_1$  or  $a'_2 \rightarrow e'_1$  or  $a'_1 \rightarrow a''_1$ ) (Table 2).

Band 6\_C<sub>70</sub> at 2.804 eV was observed in the absorption spectra of the C<sub>60</sub>/C<sub>70</sub> films with  $d = 25, 35,$  and 100 nm. The relative intensity of this band is maximum for the 25-nm C<sub>60</sub>/C<sub>70</sub> film and does not change for the 35- and 100-nm films (Table 4, row 7; Table 3, row 7).

Band 7\_C<sub>70</sub> at 3.018 eV was observed in the absorption spectra of the C<sub>60</sub>/C<sub>70</sub> films with  $d = 25, 35,$

and 100 nm. The relative intensity of this band decreases with the growth of the C<sub>60</sub>/C<sub>70</sub> film thickness (Table 4, row 8; Table 3, row 9).

Band 8\_C<sub>70</sub> at 3.252 eV was observed in the absorption spectra of the C<sub>60</sub>/C<sub>70</sub> films with  $d = 25, 35,$  and 100 nm. Its relative intensity does not change, as the thickness of C<sub>60</sub>/C<sub>70</sub> films changes (Table 4, row 9; Table 3, row 11). According to the position of its peak, this band is close to band C<sub>70</sub> at 3.211 eV (the  $e'_2 \rightarrow e'_1$  or  $a'_2 \rightarrow e'_1$  or  $a'_1 \rightarrow a''_1$  transition) (Table 2).

In the absorption spectra of the C<sub>60</sub>/C<sub>70</sub> films, band 9\_C<sub>70</sub> at 3.531 eV is absent (Table 4, row 11). We may assume that this band does not manifest itself against the background of intense C<sub>60</sub> components at 3.440 and 3.640 eV. According to the position of its maximum, this band is close to the C<sub>70</sub> band at 3.595 eV (the  $e'_1 \rightarrow e'_2$  transition) (Table 2).

Therefore, the above data confirm the presence of the C<sub>70</sub> component in the C<sub>60</sub>/C<sub>70</sub> films with the thicknesses  $d = 25, 35,$  and 100 nm. The calculated average values of the transition energies and relative intensities (in parentheses) of bands 5\_C<sub>70</sub>, 6\_C<sub>70</sub>, 7\_C<sub>70</sub>, and 8\_C<sub>70</sub> in the spectra of the C<sub>60</sub>/C<sub>70</sub> films with  $d = 25, 35,$  and 100 nm are 2.652 eV (0.099), 2.849 eV (0.101), 3.050 eV (0.109), and 3.245 eV (0.127), respectively. They agree well with the following data obtained for the 20-nm C<sub>70</sub> films: 2.594 eV (0.110), 2.840 eV (0.083), 3.018 eV (0.147), and 3.252 eV (0.188), respectively (Tables 3 and 4). Therefore, the bands at 2.474, 3.440, and 3.640 eV can be used to identify C<sub>60</sub> in the fullerene mixture films on the basis of their absorption spectra. The relative variations of the energy of the C<sub>70</sub> peaks at 2.594, 2.804, 3.018, and 3.252 eV in the spectra of the C<sub>60</sub>/C<sub>70</sub> films with  $d = 25, 35,$  and 100 nm are as follows: 3.1%, 2.5%, and 1.2%, respectively, for the peak at 2.594 eV; 2.4%, 1.6%, and 0.8%, respectively, for the peak at 2.804 eV; 1.6%, 0.4%, and 1.1 %, respectively, for the peak at 3.018 eV; and -0.2%, -0.9%, and 0.5%, respectively, for the peak at 3.252 eV.

The variations in the relative intensities of the C<sub>60</sub> and C<sub>70</sub> bands in the absorption spectra of the C<sub>60</sub>/C<sub>70</sub> films allow us to assume that both components sublimated at the sputtering beginning, so the C<sub>60</sub>/C<sub>70</sub> films with the thicknesses  $d \leq 100$  nm were formed via the deposition of C<sub>60</sub> and C<sub>70</sub> molecules onto silica substrates. The resulting films are two-component. After a drastic reduction in the intensity



of C<sub>70</sub> sublimation because of a small amount of C<sub>70</sub> in the crucible, the C<sub>60</sub>/C<sub>70</sub> films with the thicknesses  $d > 100$  nm consist of two layers. The first 100-nm layer, which is in direct contact with the substrate, is two-component, whereas the next layer is single-component and mainly consists of C<sub>60</sub> molecules.

#### 4. Conclusions

The molecular interaction between the fullerenes and the substrates affects the structure of the C<sub>60</sub>/C<sub>70</sub> films. Polycrystalline C<sub>60</sub>/C<sub>70</sub> films with needle-like and round crystallites are formed on silica substrates with intermediate carbon or ITO layers. Quasi-amorphous C<sub>60</sub>/C<sub>70</sub> layers are formed on the surface of copper substrates, and the surface C<sub>60</sub> and C<sub>70</sub> molecules become centers of the crystallite formation.

The values of the effective absorption coefficient  $\alpha$  of the C<sub>60</sub>/C<sub>70</sub> films are estimated for various incident photon energies  $E$ . It is found that the values of  $\alpha(E)$  obtained for the C<sub>60</sub>/C<sub>70</sub> films correlate better with the  $\alpha(E)$ -values calculated for the C<sub>60</sub> films and the corresponding incident photon energies. This fact means that C<sub>60</sub> is the main component in the C<sub>60</sub>/C<sub>70</sub> films.

The nature of the C<sub>60</sub> and C<sub>70</sub> absorption bands is discussed in detail by analyzing the literature and our data. The C<sub>60</sub> absorption bands at 2.474, 3.440, and 3.640 eV and the C<sub>70</sub> absorption bands at 2.594, 2.804, 3.018, and 3.252 eV can be used to identify those substances in fullerene mixtures

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МОРФОЛОГІЯ ПОВЕРХНІ  
ПЛІВОК СУМІШІ ФУЛЕРЕНІВ  $C_{60}/C_{70}$ .  
ІДЕНТИФІКАЦІЯ  $C_{60}$  ТА  $C_{70}$  У ПЛІВКАХ  
 $C_{60}/C_{70}$  ЗА ЇХ СПЕКТРАМИ ПОГЛИНАННЯ

Плівки суміші  $C_{60}/C_{70}$  наносили на різні підкладки методом термічної сублімації у вакуумі 6,5 мПа. Досліджено морфологію поверхні плівок  $C_{60}/C_{70}$  товщиною 195 нм. Встановлено, що на кремнеземних і мідних підкладках формуються полікристалічні і квазіаморфні плівки  $C_{60}/C_{70}$ , відповідно. Природа смуг поглинання  $C_{60}$  і  $C_{70}$  була детально обговорена на основі аналізу літератури та наших даних. Спектри поглинання плівок  $C_{60}$ ,  $C_{70}$  і суміші  $C_{60}/C_{70}$  описувалися сумою функцій Гауса. Смуги поглинання  $C_{60}$  (2,474, 3,440 і 3,640 еВ) і  $C_{70}$  (2,594, 2,804, 3,018 і 3,252 еВ) можуть бути використані для ідентифікації цих речовин у сумішах фулеренів. Було виявлено, що  $C_{60}$  є домінуючим компонентом у плівках  $C_{60}/C_{70}$ .

*Ключові слова:* тонка плівка, морфологія поверхні, спектри поглинання, підгонка, Гаусіани, суміш  $C_{60}/C_{70}$ .