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Effect of nanosize metal overlayer on C_{60} thin film optical parameters near fundamental absorption edge

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Abstract. The effect of nanosize metal overlayer, both evaporated on C_{60} films (Bi, In) and attached as nanoparticles of (Ag, Au), on the optical parameters of C_{60} films near the fundamental absorption edge has been studied. The values of direct band gap (E_g), the optical gap (E_o) in the framework of Tauc model and the Urbach tail parameter (E_U) were determined from the absorption coefficient (α) spectra plotted in coordinates $(\alpha h\nu)^2$, $(\alpha h\nu)^{1/2}$, $\ln(\alpha)$ vs $h\nu$, respectively. Parameters obtained testify diminishing the structural disorder in C_{60} thin films with nanosize metal overlayer at optimal ratio of C_{60} to metal layer thicknesses.

Keywords: C_{60} fullerene film, metal nanolayer, optical parameters, fundamental absorption edge.

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1. Introduction

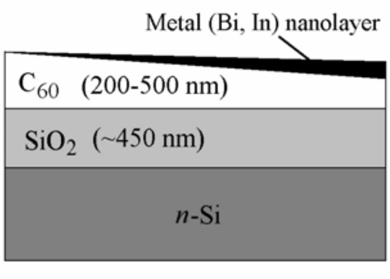
The perspectives of using C_{60} thin films in optical and electronic devices require the knowledge of the dependence of their optical parameters on the heterostructures composition (substrate and overlayer), conditions of their manufacturing and subsequent operation or modified treatments. The optical absorption band gap of C_{60} films was shown to depend on their degree of crystallinity [1] that in turn can be dependent both on the deposition conditions and on the internal mechanical stresses [2] in heterostructures. The C_{60} film growth under vacuum evaporation starts as islands, but with increasing the film thickness both the grains shape and size are dependent on the type of substrate material (amorphous or crystalline), its temperature and evaporation rate [3]. At room temperature of substrates, a polycrystalline grain structure with random orientation is realized. With increasing the substrate temperature, the mechanism of C_{60} film growth and its morphology are strongly affected by the strength of the C_{60}-substrate interaction, the lattice misfit at the interface and by the mismatch in the thermal expansion coefficients, leading to the internal stresses in heterostructure. Mechanical stresses in C_{60} films depend both on their thicknesses, diffusion of impurities or polimerized modification of C_{60} and on the stresses at the C_{60} films/overlayer (specifically metal) interface, which, in turn, affects on the energy-level diagram.

In this work, we investigate the effect of nanosize metal overlayer on optical properties of C_{60} films near the fundamental absorption edge (conditioning their photosensitivity edge spectra) in dependence both on the metal type and on the C_{60} film thickness and its modification as well as on the substrate type (Si or SiO_2/Si). The energetic parameters of the C_{60} film absorption edge, namely: the direct band gap (E_g), optical gap (E_o) in the framework of the Tauc model and Urbach tail parameters (E_U) were determined from the absorption coefficient (α) spectra plotted in coordinates $(\alpha h\nu)^2$, $(\alpha h\nu)^{1/2}$, $\ln(\alpha)$ vs $h\nu$, respectively, just as in [4, 5].

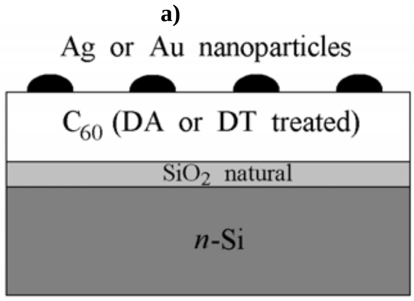
2. Experimental details

The C_{60} films of thicknesses from 100 to 500 nm were deposited on Si or SiO_2/Si substrates by vacuum thermal evaporation without heating the substrates. Two types of investigated structures are shown in Fig. 1. In one of them (a), the C_{60} layer was evaporated on the thermally oxidized Si surface, and subsequent evaporations of metal (Bi or In) nanolayers with thicknesses ≤1.5 nm were carried out in such a way, that their thicknesses decreased with an increase of C_{60} layer thickness. In the other type of structures (b) the thin (~100 nm) C_{60} layers were evaporated on *n*-Si substrate, chemically modified with 1,8-diaminooctane (DM) or 1,8-dithioloctane (DT) acting as a cross-linking agents, capable of stable binding the Ag or Au nanoparticles, respectively [6, 7] on C_{60} surface.

The C_{60} film thickness value and spectra of its effective optical parameters (refractive index *n* and extinction coefficient *k*, used for calculations of α) were determined from the reflectance spectra measured within the wavelengths range λ = 400…1100 nm ($h\nu$ = 1.1…3.1 eV) at variable angles of incidence of *p*- and *s*-polarized light, by fitting experimental dependences with the theoretical ones. They were calculated within the framework of a one-layer model in the case of too thin or noncontinuous (island) metal film (Fig. 2) or two-layer (C_{60}-In) model (Fig. 3).



a)



b)

Figure 1. Schemes of investigated structures.

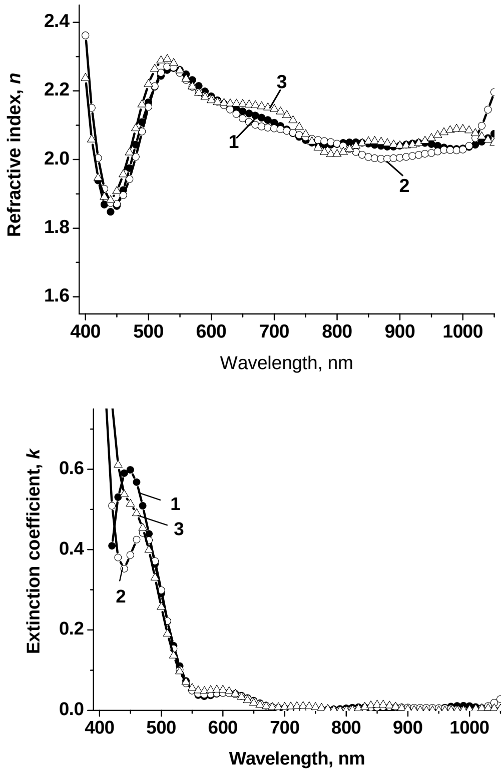


Fig. 2. Spectral dependences of optical parameters (*n*, *k*) of Bi/C_{60} layers with determined thicknesses, nm: 499 (*1*), 397 (*2*), 283 (*3*).

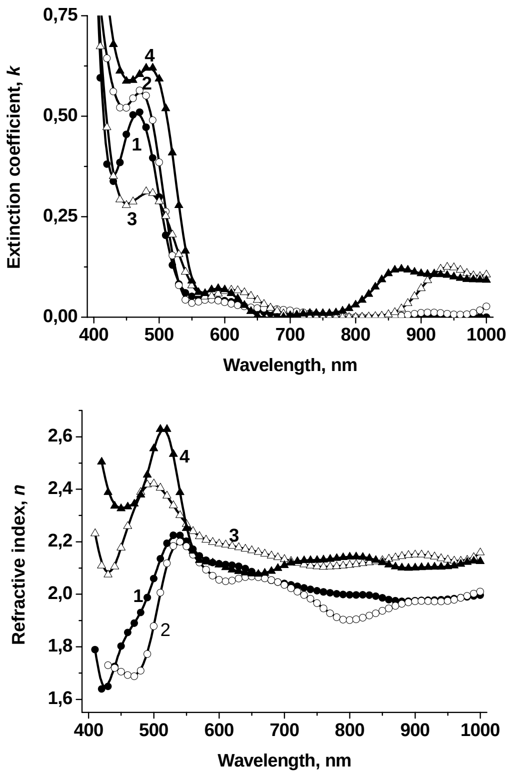


Fig. 3. Spectral dependences of optical parameters (*n*, *k*) for C_{60} layers of In/C_{60}/SiO_2/Si structure with determined In/C_{60}, thicknesses, nm: 0.03/426 (*1*), 0.1/351 (*2*), 1.0/259 (*3*), 1.51/229 (*4*).

3. Results and discussion

The spectral dependences of the absorption coefficient $\alpha = 4\pi k/\lambda$ for the investigated C_{60} films, plotted in coordinates $(\alpha h\nu)^2$, $(\alpha h\nu)^{1/2}$, $\ln(\alpha)$ vs $h\nu$ (Figs 4 and 5), allowed to determine the values of their direct band gap (E_g), of the optical gap (E_o) according to the Tauc model and Urbach tail parameter (E_U), respectively. Parameters obtained are presented in Tables 1 to 3.

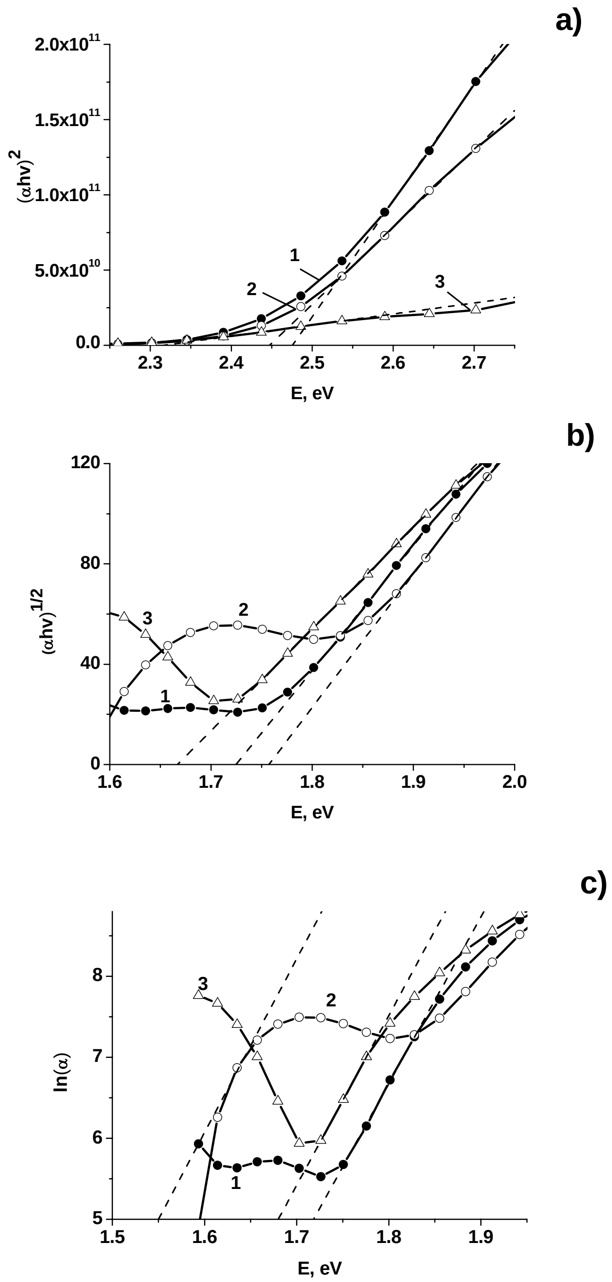


Fig. 4. Spectra of the light absorption coefficients α in coordinates $(\alpha h\nu)^2$, $(\alpha h\nu)^{1/2}$ and $\ln(\alpha)$ vs $h\nu$ for Bi/C_{60} films with the thicknesses, nm: 499 (*1*), 283 (*2*), and 242 (*3*).

Table 1. The optical absorption edge parameters for Bi/C_{60} films.

No.	*d*, nm (C_{60})	E_g, eV	E_o, eV (Tauc gap)	E_U, meV (Urbach tail parameter)
1	499±1	2.47±0.02	1.73±0.02	49±2
2	329±1	2.44±0.02	1.79±0.02	47±2
3	283±1	2.45±0.02	1.76±0.02	47±2
4	242±1	2.32±0.02	1.67±0.02	48±2

Table 2. The optical absorption edge parameters for C60 films of In/C60/SiO2/Si structure.

No.	In	C_{60}			
	d, nm	*d*, nm	E_g, eV	E_o, eV (Tauc gap)	E_U, meV (Urbach tail parameter)
1	0.03±0.02	426±1	2.43±0.02	1.73±0.02	37±2
2	0.1±0.02	351±1	2.42±0.02	1.58±0.02	25±2
3	1.0±0.02	259±1	2.32±0.02	1.71±0.02	27±2
4	1.5±0.02	229±1	2.33±0.02	1.85±0.02	40±2

Table 3. The optical absorption edge parameters for chemically modified C_{60} films and further decorated with metal nanoparticles.

Structure	d_1, nm	E_g, eV	E_o, eV	E_U, meV
C_{60}-DA/Si	122±1	2.36±0.01	1.59±0.01	25±1
C_{60}-DA-Ag/Si	122±1	2.33±0.01	1.48±0.01	16±1
C_{60}-DT/Si	82±1	2.35±0.01	1.62±0.01	29±1
C_{60}-DT-Au/Si	90±1	2.32±0.01	1.53±0.01	23±1

It is seen that optical parameters of C_{60} thin films near the fundamental absorption edge are affected not only by the C_{60} deposition rate and substrate temperature [1, 4, 8], but also by mechanical stresses in heterostructure, dependent on substrate crystallinity (Si or SiO_2 in our case) and the C_{60} film thickness. The decrease of the near-edge optical absorption parameters of C_{60} films deposited on thermally oxidized Si substrate was observed in the case of nanosize (≤1 nm) metal overlayer. Specifically, $E_g = 2.32\pm0.02$ eV was obtained for C_{60} layer thickness of ~240 nm (Bi) or ~260 nm (In) with respect to $E_g = 2.44\pm0.03$ eV for the films with greater ratios of C_{60} to metal layer thicknesses. Simultaneous decrease of E_o from (1.75±0.04) eV to 1.67 eV was observed for C_{60}/Bi film. For C_{60}/Si structures with C_{60} films (thickness of ~100 nm)

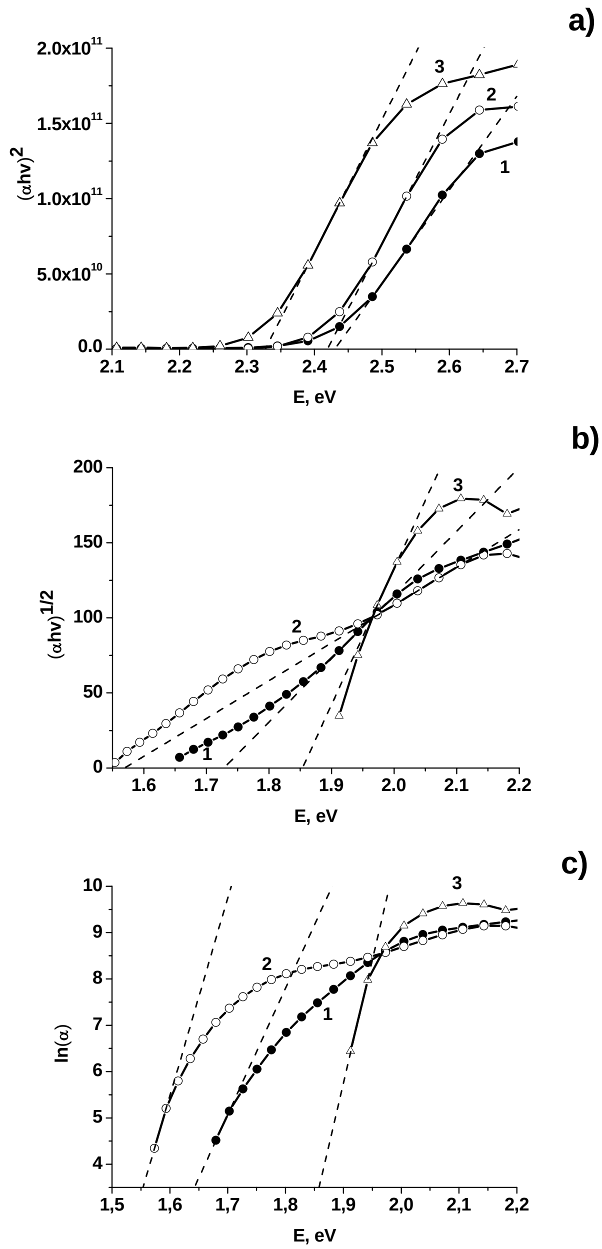


Fig. 5. Spectra of the light absorption coefficients α in coordinates $(\alpha h\nu)^2$ $(\alpha h\nu)^{1/2}$ and ln(α) vs $h\nu$ for C_{60} layers of $In/C_{60}/SiO_2/Si$ structure with determined In/C_{60}, thicknesses, nm: 0.03/426 (*1*), 0.1/351 (*2*), 1.51/229 (*3*).

modified with 1,8-diaminooctane or 1,8-dithioloctane, the decrease of all optical parameters (E_g, E_o, E_U) was found after deposition of Ag or Au nanoparticles, respectively.

Thus, the found effect of nanosize metal overlayer on optical parameters of C_{60} thin films near the fundamental absorption edge at optimal ratio of C_{60} to metal layer thicknesses testifies diminishing of all energetic parameters (E_g, E_o, E_U) of thin C_{60} films, while the higher parameter values may be caused by both structural disorder in C_{60} films and internal mechanical stresses in the heterostructure.

4. Conclusions

The analysis of the absorption coefficient spectra near the fundamental absorption edge for the investigated thin C_{60} fullerene films allowed us to determine the influence of nanosize metal overlayer on their energetic parameters (the direct band gap, the optical gap in the framework of the Tauc model, and the Urbach tail parameter), the values of which depend on the degree of C_{60} films crystallinity and mechanical stresses in heterostructure.

Diminishing all the energetic parameters of C_{60} films, determined in the framework of one- or two-layer model, was found for all the investigated metal (Bi, In, Au, Ag) overlayers, but their optimal thicknesses were shown to depend on the initial parameters of C_{60} layers, the more high values of which were caused by structural disorder in C_{60} films and internal mechanical stresses in heterostructures.

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