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Modification of the Properties of Carbon Films for Photovoltaic Converters

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The semiconductor materials with the values of energy band gap in the range of 1-2 eV are the most suitable for manufacturing solar cells. These objects include some of the carbon allotropic modifications, as well as quantum dots on the surface of these materials, which act as the basis for the creation of new optoelectronic devices based on nanostructures. This paper presents the investigations of the optical properties and structure of the synthesized multilayer system diamond-like carbon film/carbon quantum dots/C_{60}film (DLC/Qdots/C_{60}).

Keywords: Fullerene, Diamond-like carbon films, Quantum dots, Absorption spectra, Energy transitions.

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1. INTRODUCTION

Utilization of semiconductor photoelectric transducers (PET) is the most effective way of the solar energy conversion, since this is a direct single-stage energy transition [1].

Semiconductor materials with the values of the band gap energy in the range of 1-2 eV are the most applicable for the solar cell production. At the present time, an interest to the carbon-based materials, in particular, to C_{60} films and diamond-like carbon (DLC) films for use in such elements and other electron devices, increases [2].

Fullerene C_{60} films and structures on their basis can possess high efficiency of the energy conversion due to the ultrafast transfer of photoinduced charge. Crystals and thin films of pure C_{60} are similar by the optical and electronic properties to the *n*-type semiconductors and simultaneously they remain the features connected with molecular structure. It is established that the band gap width of fullerene C_{60} is equal to ~ 1,6 eV. This parameter can be changed depending on the molecular symmetry [3].

Besides fullerite, DLC films are the promising material for the formation of functional layer in photoelectric transducers [4]. Such films are of great interest due to the particular combination of the properties: high hardness, low friction coefficient, transparency in the IR spectral region, possibility of variation of the band gap width and conduction type depending on the synthesis conditions and during doping. Deposition of accelerated fullerene molecules from the ionized or neutral beam is one of such synthesis methods.

Formation of quantum dots with typical sizes from units to tens of nanometers in all three dimensions is possible in the stated carbon films. When linear sizes of the spatial localization region of particles become less than their mean free path in unlimited material, effect of the dimensional quantization of the energy spectra of these particles appears. Such low-dimensional systems are the basis for the creation of new optoelectronic devices based on nanostructures.

In the present work, we investigate the optical properties and structure of the synthesized multilayer system DLC film/carbon quantum dots/fullerene C_{60} film (DLC/Qdots/C_{60}).

2. MATERIALS AND INVESTIGATION TECHNIQUES

For the production of C_{60}, DLC films, and quantum dots as a source of the material, powder of fullerene C_{60} with the purity of 99,5% (NeoTechProduct, Saint-Petersburg, Russia) was used. Fullerene powder was purified by vacuum distillation before use.

DLC films were obtained by deposition from mass-separated ion beam with the average C_{60} ion energy of $E = 5$ keV at the substrate temperature of $T_s = 100$ °C. Quantum dots were obtained on the DLC film at the temperature of $T_s = 400$ °C from the beam of accelerated C_{60} ions with the energy of 5 keV. It is assumed that one C_{60} ion at collision with the surface forms a quantum dot. C_{60} films were produced by means of the vacuum thermal deposition.

Microscopic investigations of the structure of the obtained DLC films were carried out on the transmission electron microscope PEM-125K with the resolution of 0,2 nm. Preparation of the samples for PEM was performed by the chemical etching of silicon substrate in acid mixture HF:HNO_3 = 1:10 after film deposition, then films were washed in deionized water and placed on copper grid.

The nanohardness and modulus of elasticity of DLC films were measured by nano-indenter MTC G200 with use of the diamond Berkovich tip ($R < 20$ nm). The technique of continuous scan in depth was applied and this allowed to register modulus of elasticity and hardness depending on the indenter penetration depth.

Measurement of the Raman scattering spectra was performed in the backscattering geometry using device JY LabRam HR equipped by CCD detector with cooling by liquid nitrogen. Spectra were obtained with the use of the line 514,5 nm of argon-ion laser.

Measurements of the optical characteristics of C_{60}, DLC films, and multilayer system with quantum dots were carried out using the spectrophotometer SF-26 in the wavelength range of $\lambda = 300$-1200 nm. The spectral dependences of the reflection $R(\lambda)$ and transmission $T(\lambda)$ coefficients were taken. In order to eliminate the influence of glass substrate when taking the spectra of $T(\lambda)$, a substrate without film was installed into the comparison channel.

3. RESULTS AND DISCUSSION

The spectral dependences of the reflection $R(\lambda)$ and transmission $T(\lambda)$ coefficients were obtained for C_{60} and DLC films. The films have shown a sufficiently high transparency in the IR and visible spectral regions.

To determine the band gap optical width E_g of C_{60} and DLC thin films we have used the following correlation which is valid for direct band-gap semiconductors:

$$\alpha h\nu = A(h\nu - E_g)^{\frac{1}{2}}, \quad (1)$$

where A is a some constant depending on the effective mass of charge carriers in material; $h\nu$ is the energy of optical quanta; α is the absorption coefficient of material.

It follows from this correlation that extrapolation of the linear part of the graph on the energy axis allows to define the band gap width of semiconductors. Absorption coefficients of the films at different lengths of incident radiation, necessary for the calculation of E_g, were obtained by the transmission and reflection spectra with the use of the relation

$$\alpha = -\frac{1}{d}\ln\left(\frac{1}{R^2}\left(-\frac{(1-R)^2}{2T} + \sqrt{\frac{(1-R)^4}{4T^2} + R^2}\right)\right). \quad (2)$$

As the calculations show, absorption coefficient of the obtained C_{60} films in the region of radiation energies which exceed the band gap is $\alpha = (1 \times 10^4\text{-}7 \times 10^5)$ cm^{-1}. For the DLC films it equal to $\alpha = (7 \times 10^4\text{-}3 \times 10^5)$ cm^{-1}.

In Fig. 1 we show the dependences of the absorption coefficient in the coordinates $(\alpha h\nu)^2 - h\nu$ which were used for the determination of the band gap width of C_{60} and DLC films. As seen from the figure, these dependences in the range of energies close to the photoelectric threshold are approximated by straight lines and their intersection with the energy axis allows to define E_g.

Three typical energy transitions were fixed on the spectrum of C_{60} film (Fig. 1a) [5, 6]. Calculation of the transition energy gave the following values: E_{g1} = 1,7 eV, E_{g2} = 2,6 eV, E_{g3} = 3,1 eV. Transition E_{g1} with the energy of 1,7 eV corresponds to the band gap width of C_{60} film. The given film exhibited photoresistive properties.

According to the calculations for DLC films, the band gap width E_g was equal to 2,5 eV (Fig. 1b). Based on the data of electronography and electron microscopy, the DLC films obtained at the substrate temperature of 100 °C and mean ion energy of 5 keV had amorphous structure and weakly developed surface relief. Thus, we have fixed wide halo corresponding to the diamond-like phase (see Fig. 2).

The fact that films obtained at 100 °C and E = 5 keV had the diamond-like structure is also confirmed by the investigation results by the method of the Raman scattering spectrometry which has shown a considerable fraction of sp^3-bonds (up to 80%), as well as by the nanoindentation of thick films (t = 1 μm) deposited on silicon. Mean value of the nanohardness of DLC film was equal to 46 GPa, and of the Young's modulus – 336 GPa [7].

Quantum dots were obtained on the studied DLC film at the substrate temperature T_s = 400 °C from the beam of accelerated C_{60} ions with the energy of 5 keV. It was established beforehand that annealing of DLC film itself at T = 400 °C does not change its structure. Then, thin film of fullerene C_{60} was deposited on the DLC/Qdots system by the vacuum thermal sputtering. Two systems with quantum dots (DLC/Qdots/C_{60}) and without them (DLC/C_{60}) were obtained for the optical investigations in a single technological cycle.

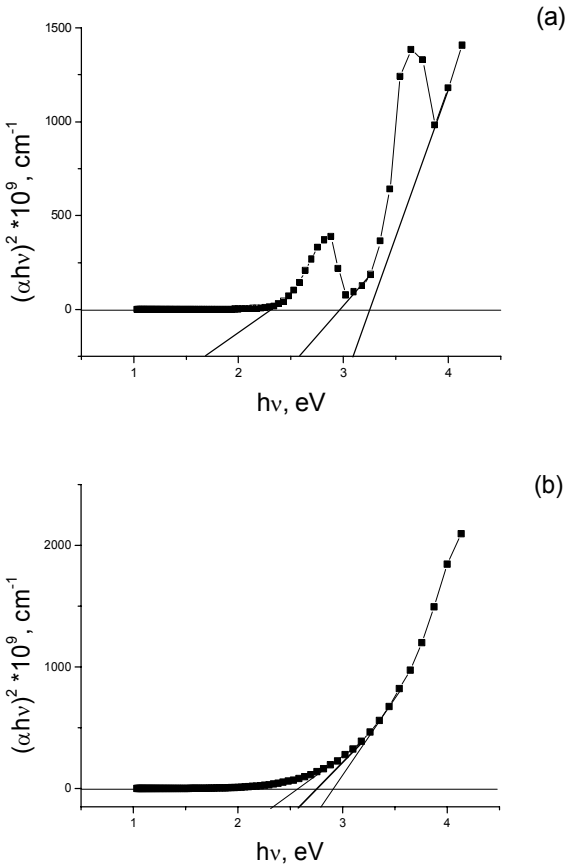

Fig. 1 – Determination of the band gap optical width: C_{60} film (a) and DLC film (b)

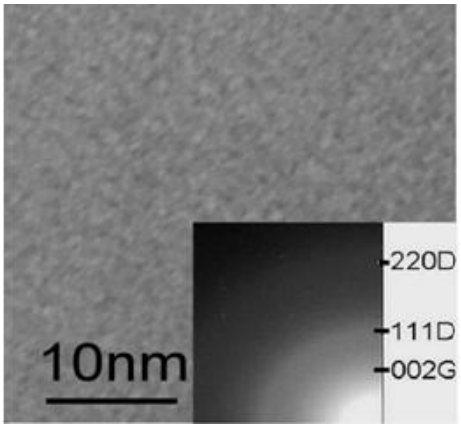

Fig. 2 – Microscopic image and electron diffraction pattern of the DLC film obtained at E = 5 keV and T_s = 100 °C

5 energy transitions with the energies of E_{g1} = 1,7 eV, E_{g2} = 2,18 eV, E_{g3} = 3 eV, E_{g4} = 3,8 eV, and E_{g5} = 4,3 eV (Fig. 3) were fixed on the absorption spectrum of the synthesized DLC/Qdots/C_{60} system.

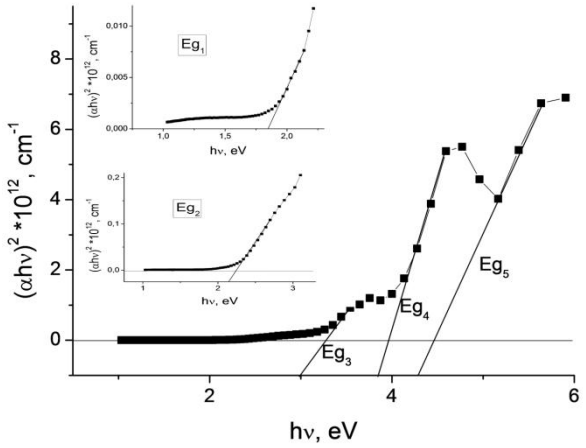

Fig. 3 – Determination of the band gap optical width of the DLC/Qdots/C_{60} system layers

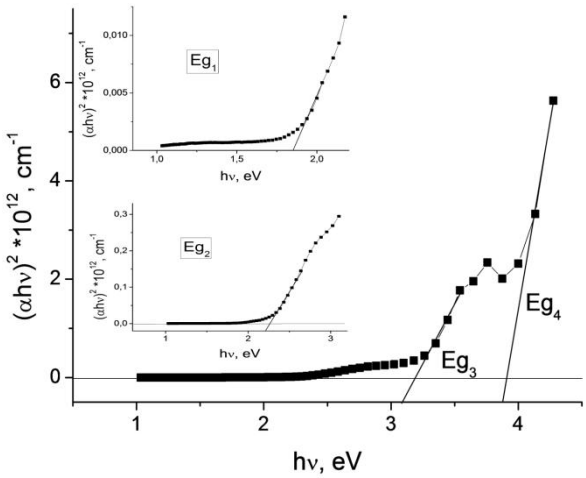

Fig. 4 – Determination of the band gap optical width of the DLC/C_{60} system layers

Transitions 1, 3, 4 are typical for the C_{60} film, and transition 2 corresponds to the band gap width of the DLC film. While on the absorption spectra of the system without quantum dots (DLC/C_{60}) transitions 1, 2, 3, 4 remain, transition 5 is absent (see Fig. 4). For better visualization of the energy transitions Eg_1 and Eg_2 for both multilayer systems in Fig. 3 and Fig. 4 we present increased images of the corresponding spectral regions.

Therefore, transition E_{g5} with the energy of 4,3 eV indicates the presence of an additional structure in the system with quantum dots.

4. CONCLUSIONS

In the work, we have investigated the transmission and reflection coefficients of fullerene C_{60} thin films and DLC films based on which we have calculated the absorption spectra and band gap optical widths of the materials. According to the calculations, the band gap optical width for C_{60} film is equal to ~ 1,7 eV, and for DLC film – ~ 2,5 eV.

Based on the electronography and electron microscopy data, the DLC films obtained at the substrate temperature of 100 °C and mean ion energy of 5 keV have the amorphous structure and weakly developed surface relief. A contrast typical for amorphous films was seen on the surface images, and microdeformation represented two halos with maximums typical for amorphous carbon.

Based on the studied C_{60} and DLC films, two multilayer systems were obtained in a single technological cycle with quantum dots (DLC/Qdots/C_{60}) and without them (DLC/C_{60}), for which the absorption spectra were calculated and the presence of an additional structure with E_{g5} = 4,3 eV was established in the system with quantum dots.

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