Optical spectroscopy of organic materials based on C_{60}<A_2B_6>

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Abstract. The structure, optical and photoelectrical properties of thin films based on C_{60}<A_2B_6> materials are studied. Reproducible vacuum method of thin fullerene films production with Cd<Te;S> impurity on Si, glass and mica surfaces are developed. Surface morphology of the films are investigated by AFM and SEM methods. The *ab initio* quantum-chemical calculations of the geometry, total energy, excited states energy of supramolecules complex fullerene-cadmium telluride are performed. Optical absorption spectra in UV and visible regions, Raman and photoluminescence spectra are studied. Comparing to a pure fullerene, the additional absorbance and luminescence peak at 600 nm are observed. The intensity of additional peaks are defined as the charge composition as a type of substrate. These results are interpreted as an appearance of the dipole-allowed transitions in the fullerene excited singlet states spectrum due to an interference with cadmium telluride.

1. Introduction

Organic/inorganic mixed nanocomposites promise to be valuable to solar energy conversion, photovoltaics, specifically to novel light-driven systems [1]. New composite materials based on C_{60} fullerene as well as nonorganic semiconductor nanoparticles A_2B_6 are a great interest [2]. The properties of hybrid materials can be regulated via a variety of functional groups, which can be incorporated in the organic C_{60} matrix. Photovoltaic devices, sensors, opto-electronics, etc. might represent some of the most important applications of these novel materials. In this work thin films of new hybrid organic-inorganic semiconductors, exhibiting photoconductive properties have been produced by simple vacuum method. Molecular semiconductor materials have been studied for more than a half century because they have high potential for unique device applications such as light-emitting diodes, solar cells, and field-effect transistors with low cost, low weight, and mechanically flexible electronics. Therefore development of composite electronic and photoelectronic materials and structures based on C_{60} are relevant and important. In the last years many studies have been focused on optical characteristics of both C_{60} molecules and solid fullerite. Frenckel exciton formation takes place as a result of light quant absorption by C_{60} molecule. It is necessary to separate excitons to get photovoltage. Geterojunction of donor and acceptor materials may observe this function very effective, because it provide with charge transfer mechanism between molecules. It was found that fullerene C_{60} is a strong electron acceptor. Conjugated polymers, phthalocyanines, materials from porphyrin class and also nonorganic semiconductor from A_2B_6 group are effective donors. Therefore nanostructured material contacts with fullerene are considered as a possible material for solar cell creation. Nevertheless, the main property which has to be taken into account when we use organic structures is their quick degradation under the influence of oxygen or H_2O vapor. This aspect reduces to comparatively short useful time of those devices. Therefore intensive research in the field of
composite organic and nonorganic semiconductor, which includes C$_{60}$-CdTe films, structures is underway. It is done to increase the lifetime of organic solar cells. CdTe is a well-known material for photovoltaic because. It is a direct-gap semiconductor with 1.5 eV energy band gap. This band gap is optimal for absorption of sunlight, because increasing band gap lead to decrease covered the solar spectrum. Decreasing band gap leads to leaving of a portion of absorbed photons to intraband scattering and solar cell heating.

2. Methods of obtaining and experimental research of samples
Thin nanocomposite films from composite mixture of fullerene C60 (99.98%) and inorganic donor CdTe(S) were prepared by vacuum evaporation method on a pre-heated in a height vacuum up to 150°C glass/indium tin oxide, silicon (111) and KBr substrates [3]. Two different techniques - quasi-closed volume (QCV) and Knudsen cell are used, films thickness was 200-500 nm. In the case of QCV method it was provided a full initial charge mixture transfer to the substrate in the process of sublimation. A Knudsen cell evaporation method is a sophisticated method of evaporation from molecular beam. In comparison with the initial charge it can lead to a significant changing of a film composition. Obtaining a large area film possibility is an advantage of the Knudsen cell. Evaporation was produced on a pre-heated in a height vacuum up to 150°C glass/indium tin oxide, silicon (111) and KBr substrates in both methods. Then substrates were cooled to 40°C. The result is random distribution of acceptor and donor materials in amorphous films. Films prepared at 500-550°C of the evaporator temperature from C$_{60}$ and CdTe mixture in various percentage (10–50%). The films composition and surface morphology was studied SEM-EDAX and AFM methods. A scanning electron microscope Jeol JSM-6390 was used to study the surfaces’ morphology. It worked with resolution of 3 nm. The films composition in the selected area was measured by energy dispersive microanalysis console “Oxford INCA Energy” with the utmost sensitivity 0.1%. Films’ surfaces and composition of components were studied by electrons with 8 KeV energy. Raman spectra were measured by "Mikroraman" from Renishaw device at 512 nm wavelength. The power of exiting beam was set of 0.1 mW/mcm. It was done to account an oxidation and photopolymerisation effects in films. Measuring time (and the laser irradiation time accordingly) were varied from 30 sec to 30 min. Photoluminescence spectra were measured by using automated installation based on Horiba Jobin Yvon spectrometer. It is composed of FHR 640 monochromator with a grating of 1200 mm$^{-1}$ and the Symphony II (1024*256) Cryogenic Open - Electrode CCD detector. . Excitation of photoluminescence was produced by continuous semiconductor laser with 410 nm wavelength, 50 mW powerty. Filter was installed before the slit of the monochromator to avoid scattering laser radiation falling into the monochromator. CCD chamber was maintained at the temperature of 77 K. Ellipsometry spectra were obtained using an Alpha - SE Wolland ellipsometer with fixed incidence angle of 70 ° and a wavelength from 380 to 890 nm. Inverse problem solution was performed using the CompleteEASE considering the surface roughness and the Kramers-Kronig method B - spline.

3. Experimental results and discussion
The surface topography of all samples was measured by scanning electron microscope. Irregularities in films composition (phase contrast) weren’t detected until the limit of the microscope resolution (10 nm). Typical surface topography is shown in fig. 1. The film surface generally smooth with unique (fraction 2 and 6) in the field 100×100 mkm. Also chemical compositions spectra were measured by energy dispersive consoles (table 1). The silicon substrate is present in the spectrum due to the fact that the absorption of electrons and output of x-ray radiation is possible from the substrate when the films thickness is about 200 nm. Spectrum doesn’t contain CdTe in the center of the defect on the point 6. The defect size is about 3 mkm. It can be the inclusion of fullerene mixture with a thickness about 2mkm. Point 2 is partly gone from the fullerene crystallite and contains some CdTe. Other points (3, 4, 5) selected on a smooth homogeneous surface show sufficiently good uniformity of composition with an average content value of Cd – 1.60, Te – 1.76%.
Figure 1. SEM surface image of sample containing 15% of CdTe

Table 1. Films homogeneity composition analysis based on EDAX results.

| Spectra  | C    | O    | Si   | Cd  | Te  | Total |
|----------|------|------|------|-----|-----|-------|
| Spectrum 1 | 40,49 | 0,93 | 55,31 | 1,00 | 2,27 | 100,00 |
| Spectrum 2 | 77,09 | 1,22 | 19,83 | 0,74 | 1,12 | 100,00 |
| Spectrum 3 | 59,09 | 0,92 | 36,38 | 1,65 | 1,96 | 100,00 |
| Spectrum 4 | 59,12 | 0,77 | 37,1  | 1,44 | 1,58 | 100,00 |
| Spectrum 5 | 59,41 | 0,79 | 36,37 | 1,68 | 1,74 | 100,00 |
| Spectrum 6 | 88,3  | 1,53 | 10,18 |     |     |       |

Given the molar mass of Cd and Te, it is possible to conclude that CdTe generally is included in the composition the molecular form with some depletion of Cd.

Table 2. Films composition in comparison with the initial charge composition based on EDAX results.

| Evaporation method | Knudsen cell | QCV |
|--------------------|-------------|-----|
| CdTe weight percents in initial charge, % | 67          | 50  | 33  | 20  | 50  |
| CdTe weight percents in thin films, %     | 27          | 13  | 5-7 | 3   | 50  |

Comparative characteristics of different samples are shown in table 2. The weight percentages composition of CdTe was determined from measured chemical composition data by subtracting the effect of silicon. It may be concluded that Knudsen cell evaporation leads to significant decreasing content of CdTe in the films in comparison with the original composition. This fact can be explained by difference in condensation and re-evaporation coefficients our materials, because the saturated vapor pressure of CdTe and C$_{60}$ in this temperature range is the almost same. On the other hand evaporation in a quasi-closed volume (QCV-method) leads to a complete preservation of original charge. Moreover this method allows to obtain thicker films. Different authors observed a wide range of C$_{60}$ photoluminescence with some maxima with different relative intensity: about 720 nm (1.7 eV) and about 800 nm (1.55 eV). This range depends on rather experimental conditions which described in numerous works devoted to study of C$_{60}$ PL. Fig. 2 shows obtained PL spectra of nanocomposite fullerene films with different CdTe content. It is seen that the luminescence peak, which can be correspond to a single phase of CdTe (800 - 850 nm), is not observed. There are wide peaks, which overlaps the region 700 – 800 nm are accordingly include fullerene peaks at 720 and 800 nm.
These peaks are usually associated with $T_1 \rightarrow S_0$ transition and it's vibrations sublevels. Also there is increasing relative emission intensity at wavelength of 580 - 620 nm with the CdTe content increasing. Thereby the presence of the additional luminescence peak can be explained by change in the fullerene electron structure in the interaction with CdTe. In our opinion this peak is $S_1 - S_0$ energy transition of fullerene. We can assume that with the CdTe addition in fullerene matrix due to decrease in symmetry of fullerene molecules, and therefore partially lifted a ban on the transitions $S_1 - S_0$. This possible explanation is based on the results of quantum chemical calculations, which allowed singlet-singlet transitions for complex $C_{60}CdTe$ have energy 1.9 - 2.2 eV. Influence of gamma and X-ray irradiation on the properties, composition and structure of the samples were studied.

**Figure 2.** Photoluminescence spectra of $C_{60}(CdTe)$ samples containing various weight percentage of CdTe: 1 - 50%, 2 – 27%, 3 – 12%, 4 – 5-7%.

**Figure 3.** Photoluminescence spectra of $C_{60}(CdTe)$ samples containing 20% of CdTe on various substrates: 1,2 – on mica, 3,4 – on silicon, 2,4 – after gamma rays irradiated.
In comparison to the pure C$_{60}$ samples additional absorption and PL areas appeared in C$_{60}$-CdTe films spectra with 1.9-2.1 eV and 2.75 eV photon energy (fig. 3). The intensity of the lines depends on the content CdTe (CdS) and substrate type. Ellipsometry data allow to obtain the extinction coefficient and refractive index spectra. Fig. 4 (below) shows the extinction coefficient curves for pure fullerene sample and the sample with a high concentration of CdTe (50 mol. %). It can be seen that the sample with a high content of CdTe has an additional absorption peak at a wavelength of 630 nm, which well agrees with photoluminescence results. Increase the refractive index (Fig. 4, top) due to the fact that cadmium telluride has a large dipole moment, which polarizes the fullerene molecule from the nearest environment.

![Extinction coefficient curves for clear fullerene sample (up) and sample with a high concentration of cadmium telluride (50 mol.%)(down).](image)

### 4. Quantum-chemical calculations of C$_{60}$-A$_2$B$_6$ complexes

Quantum-chemical calculations of optimized geometry and electronic structures of C$_{60}$-CdTe complexes were performed. It was done in frame of density functional theory (DFT) with the hybrid functional B3LYP using MOLCAO-SCF method of GAUSSIAN 03 program package. The calculations were performed using the following sets of atomic Gaussian basis functions: 3-21G for carbon atoms, SBKJC VDZ ECP for cadmium and SBKJC Polarized (p, 2d)-LFK for tellurium. Many configurations, differing in initial CdTe molecules position in fullerite are considered. Calculations results for cluster C$_{60}$CdTe show that the structure has the energy minimum when tellurium atom is located above the bond 6-6 fullerene molecule at a distance of 0.22 nm. Mayer bond order for tellurium atom with the nearest carbon atoms is 0.54 and 0.60, and on the cadmium atom about 0.16 (for comparison, the order C-C bond in the fullerene molecule is equal to 1.12 for 5-6 bond, 1.38 for 6-6 bond). Energy gain in the total formation energy of such complex is 0.57 eV, it is sufficiently high to ensure the formation of the complex at room temperature. HOMO-LUMO gap is equal to 2.4 eV (for comparison, the calculation gives a molecule C$_{60}$ HOMO-LUMO = 2.9 eV, and for the molecule CdTe Eg = 1.3 eV). Energy of low-lying excited states of the electron spectrum for C$_{60}$ as and complexes of C$_{60}$-CdTe are calculated using TDDFT method. The results show that for the complexes of C$_{60}$CdTe spectrum of excited states is considerably complicated compared to the fullerene molecule and at the same time dipole-allowed singlet transitions with energies of 1.9 - 2.2 eV appear in the spectrum, which may explain the data of optical spectroscopy and luminescence.
5. Conclusions
The novel technology of thin-film composite structures based on C₆₀-CdTe is developed. Evaporation from the Knudsen cell leads to significant depletion of the CdTe-component in compare with the initial mixture. Method QCV provide completely transfer of mixture composition. SEM-EDAX investigations confirmed the presence of CdTe in all the deposited layers and consequently the preparation of a hybrid system. Comprehensive study of structure, composite and optical properties this sample led to conclusion that this method leads to molecular dispersivity of CdTe in fullerite matrix. Molecule of CdTe actively interacts with the fullerene molecules and distorts it’s symmetry. It manifests in the additional processes of emission and absorption between levels S₁ - S₀ (2.0-2.75 eV). It is assumed that this interaction may increase the probability of photoinduced charge transfer in such composite materials. The CdTe presence in these films also significantly reduces oxidation and polymerization of fullerene, which reduces degradation of the samples in the interaction with the atmosphere. Quantum-chemical calculations by the TD DFT (B3LYP) method was used to explain these results. Energy spectra of the excited triplet and singlet states for complexes C₆₀CdTe (CdS), as well as the supramolecular complexes simulating the position of the impurity molecules in the octahedral and tetrahedral interstices of the crystal lattice of fullerite are calculated. Obtained results are interpreted as an appearance of the dipole-allowed transitions in the fullerene excited singlet states spectrum due to distortions caused by intercalation CdTe in fullerite.

References

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