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V.A. AZOVSKIY,¹ V.M. YASHCHUK,¹ G.V. BULAVKO,¹ A.A. ISHCHEKNO²

¹Taras Shevchenko National University of Kyiv

(64/13, Volodymyrs'ka Str., Kyiv 01601, Ukraine; e-mail: vladimirazovskij@gmail.com)

²Institute of Organic Chemistry, Nat. Acad. of Sci. of Ukraine

(5, Murmans'ka Str., Kyiv 02660, Ukraine; e-mail: al.al.ishchenko@gmail.com)

SOME PROBLEMS IN DESIGNING A LUMINESCENCE CONVERTER FOR Si SOLAR CELLS¹

Aromatic polymer composites are characterized by the high absorption and luminescence excitation in the short-wave interval of the solar radiation spectrum from about 200 nm. Therefore, they can be used to enhance the spectral sensitivity of semiconductor solar cells, including silicon-based ones, at short waves. When such a composite absorbs light, there arise Frenkel excitons in it, which are responsible for the transfer of the excitation energy to molecular traps. The latter emit light in the spectral region of maximum solar cell sensitivity. The results obtained demonstrate a possibility to develop a luminescence converter on the basis of a polymeric composite, thus increasing the photocurrent generated by Si-based solar cells.

Keywords: luminescence converter, Si solar cell, energy transfer.

1. Introduction

The spectral sensitivity of single-crystalline silicon solar cells with one p - n -junction increases with the wavelength within the interval $\lambda = 350\div 790$ nm; then, after attaining a maximum, it rapidly decreases. This parameter has minima at wavelengths below 350 nm and above 1100 nm [1]. Even at the wavelength $\lambda = 400$ nm, the efficiency of photovoltaic radiation conversion is not high enough. The situation is even worse for CZTSSe, CZTS, and CdTe solar cells (see Fig. 1) [2].

Photons with energies below the semiconductor gap width are not absorbed. At the same time, photons with energies higher than the forbidden gap width give a small contribution to the photocurrent owing to their thermalization. In a Si solar cell, only 33% of the solar radiation energy can be used to generate the photocurrent [3]. To tackle this problem, inorganic nanoparticles or luminescent concentrators are generally applied [4].

In this work, we propose to apply a luminescent coating created on the basis of a polymer composite material and making no use of light concentrators in order to transfer the light energy from the ultraviolet

(UV) spectral interval to visible (VIS) wavelengths. This coating has to satisfy a number of requirements.

- The coating has to be transparent in the interval, where the spectral sensitivity of silicon solar cells is maximum, and it has to absorb radiation in the spectral interval $\lambda < 400$ nm;
- Since the coating is arranged on the solar cell top surface, its interaction with light has to be minimum within the solar cell absorption interval;
- The radiation losses from the coating surface should be minimized [5].

Therefore, we propose to use a multicomponent composite on the basis of polyepoxypropylcarbazon (PEPC) matrix.

2. UV to VIS Conversion

The converter has to absorb photons in the VIS and near UV spectral intervals. Photons whose energies exceed the Si band gap width ($E > 1.12$ eV) have to be transformed into photons with lower energies and absorbed in the solar cell as closer as possible to the maximum of its spectral sensitivity. Hence, high-energy photons have to be absorbed, and their energy has to be transferred to the centers that emit light

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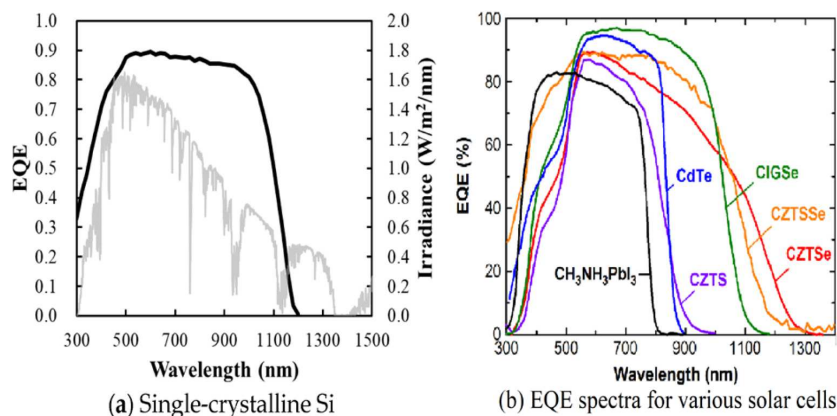


Fig. 1. Comparison of the normalized solar spectrum and the EQE spectrum of a Si solar cell (a). EQE spectra of CZTSSe-, CZTS-, CdTe-based, and other solar cells (b) [2]

in the spectral, where the silicon sensitivity is maximum. The transformed radiation is absorbed by the solar cell and induces the photocurrent.

The proposed coating should be optically inactive and should not reduce the solar cell efficiency. With this end in view, a multicomponent system was developed which absorbs photons, transfers their energy to radiative centers, and changes the radiation frequency to within the required spectral interval.

3. One-Component System

The application of the multicomponent system for the preparation of a cell coating enhances the transparency of the latter in the spectral interval, where the silicon sensitivity is maximum. Simultaneously, this system provides the radiation absorption in the short-wave interval. Therefore, the Stokes shift between the excitation and fluorescence spectra has to be rather large. It is difficult to make the Stokes shift sufficiently large (about 100 nm) for most substances. However, porphyrins (including chlorophyll) are characterized by an anomalously large shift (more than 100 nm) between the so-called Soret absorption band and the fluorescence spectrum.

Chlorophyll has two excited singlet states (S1 and S2) in the optical interval. This is why its absorption spectrum has two maxima: one of them is associated with the electron transition onto a higher energy level (S1) of the electron system, the other (S2) with the excitation of unpaired electrons in the nitrogen and oxygen atoms of the porphyrin nucleus [6]. If the electron spin does not change, the both sin-

glet states S1 and S2 are realized (the Soret band). If the electron spin changes, there arise triplets. The energy of the excited state S2 is higher, and this state is unstable. A nonradiative transition onto the excited state S1 with an energy loss of 100 kJ/mol takes place within 10–12 s. Both radiative (fluorescence or phosphorescence) and nonradiative (heat release, energy transfer to another molecule, electron transfer to another compound) transitions from the first singlet and triplet states onto the ground state are possible.

In addition, several types of chlorophyll- and carotenoid-containing pigments are involved in the photosynthesis. Their energy levels form a cascade of a peculiar kind. Owing to the transfer of the electron excitation energy along such a cascade, the shift between the absorption and fluorescence spectra of the system becomes even larger [7].

In the framework of this work, we will propose an analogous system with several absorption centers, which is transparent in the interval of the maximum spectral sensitivity of silicon. A few dyes were deposited in the PEPC matrix as impurity centers with a concentration of 1–2 wt%. The dyes were used as capture and excitation centers, which afterward emitted light in the required spectral interval.

4. Experimental Part

The signal intensity in the fluorescence spectra was measured in relative units. The obtained values were proportional to the flux of photons per 1 cm² per 1 s. All measurements were carried out on a Varian

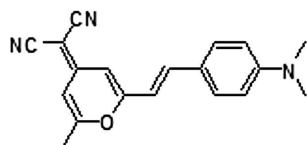


Fig. 2. Structural formula of DCM

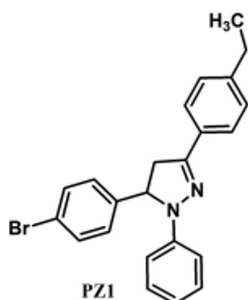


Fig. 3. Structural formula of PZ1

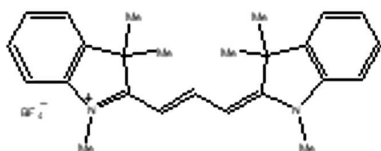


Fig. 4. Structural formula of No. 1BF₄

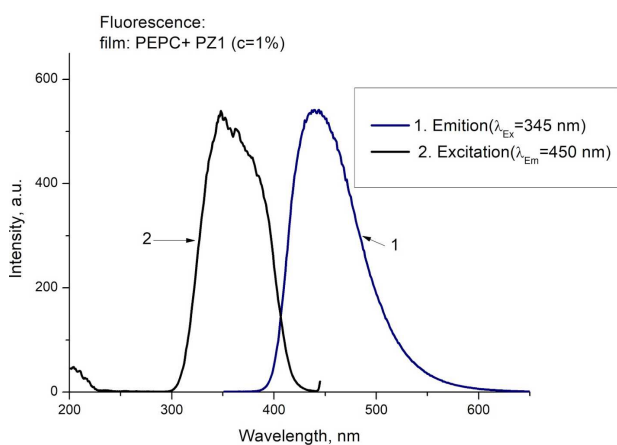


Fig. 5. Fluorescence spectrum of the film PEPC + PZ₁ (1 wt%)

Cary Eclipse fluorescence spectrophotometer at room temperature and in ambient atmosphere.

The films were fabricated by watering quartz substrates. The following substances were used as the PEPC matrix fillers:

- 5-(4-bromophenyl)-3-(4-ethylphenyl)-1-phenyl-4,5-dihydro-1H-pyrazole (PZ₁, see Fig. 2.);

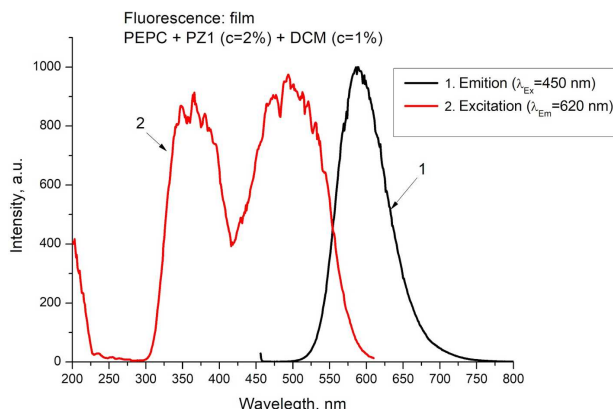


Fig. 6. Fluorescence spectrum of the film PEPC + PZ₁ (2 wt%) + DCM (1 wt%)

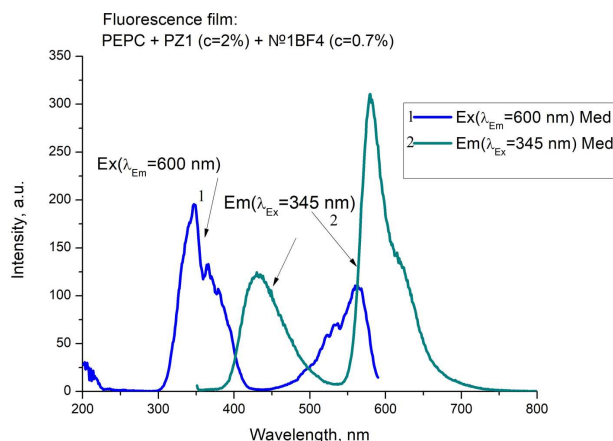


Fig. 7. Fluorescence spectrum of the film PEPC + PZ₁ (2 wt%) + No. 1BF₄ (0.7 wt%)

- (2Z)-1,3,3-trimethyl-2-[(E)-3-(1,3,3-trimethylindol-1-ium-2-yl)prop-2-enylidene]indole; tetrafluoroborate (No. 1BF₄, see Fig. 3);
- 4-(dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4H-pyran; the alternative name is 2-(2-(4-(dimethylamino)styryl)-6-methyl-4H-pyran-4-ylidene)malononitrile (DCM, see Fig. 4).

5. Fluorescence Spectra of the Molecules and Composites Used in the Luminescence Converter

The experimentally determined energies of the first excited singlet state (S₁) in the examined substances are as follows: 3.60 eV in the PEPC matrix, 3.04 eV in PZ₁, 2.42 eV in No. 1BF₄, and 2.22 eV in DCM. The results obtained made it possible to propose a cas-

cade scheme for the transfer of the energy of absorbed high-energy photons and its further reemission within the spectral interval of the maximum Si solar cell sensitivity. This scheme can increase the photocurrent yield of solar cells.

The luminescence spectra of the solid composite films of the dyes in the PEPC matrix are exhibited in Figs. 5 to 7. A structure similar to that of chlorophyll with several absorption centers and emitting light in the spectral interval of the maximum silicon sensitivity was constructed.

The relative efficiency of energy transfer from the PEPC matrix to the deposited components was determined experimentally. The integrated fluorescence intensities obtained at the excitation of the matrix and the luminescent dyes were compared. In particular, the relative efficiency of energy transfer was found to equal 63.7% for the PEPC + PZ₁ + DCM system and 75.6% for the PEPC + PZ₁ + No. 1BF₄ one.

6. Conclusions

In this work, the optical properties of solid composite films (PEPC + organic dyes) are studied. A system, similar to the chlorophyll one, containing several absorption centers and transparent in the spectral interval, where the spectral sensitivity of silicon is maximum, is created. It can be deposited on the front covering of Si solar cells to enhance the photocurrent yield. The analysis of the measured spectra confirms that the excitation energy is transferred from the PEPC matrix to the dyes, which emit light in the spectral interval of the maximum sensitivity of Si solar cells. The obtained results testify to a possibility of developing a luminescence converter for silicon solar cells in the short-wave interval.

The solar cell heating is a potential problem for the operational stability of the organic luminescence converter. In particular, to protect the coating from the thermal destruction, its thermal and mechanical contacts with a solar cell itself should be avoided. Therefore, the coating should not be deposited directly on the solar cell surface. For this reason, the thermal stability of composites was not studied in this work. On the other hand, an even higher application efficiency of the organic luminescence converter is possible for

film solar cells, which are characterized by substantial reflection losses in the short-wave interval (e.g., CIGS and CdTe).

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*В.А. Азовський, В.М. Яцук,
Г.В. Булавко, О.О. Іщенко*

ДЕЯКІ ПРОБЛЕМИ РОЗРОБКИ ЛЮМІНЕСЦЕНТНОГО ТРАНСФОРМАТОРА ДЛЯ КРЕМНІЄВИХ СОНЯЧНИХ ЕЛЕМЕНТІВ

Резюме

Для ароматичних полімерних композитів характерне значне поглинання та збудження люмінесценції в короткохвильовій області сонячного випромінювання (починаючи з 200 нм). Це дозволяє використовувати дані речовини для підвищення спектральної чутливості напівпровідникових сонячних елементів (в тому числі кремнієвих) в короткохвильовій області. В таких композитах при поглинанні світла виникають екситони Френкеля, які відповідають за перенесення енергії збуджень до центрів, які випромінюють енергію в області максимальної спектральної чутливості сонячного елемента. Отримані результати демонструють можливість розробки полімерного композитного люмінесцентного перетворювача, що може підвищити значення фотоструму в кремнієвих сонячних елементах.