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# Деякі проблеми розробки люмінесцентних трансформторів для кремнієвих сонячних елементів

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# Some problems in design of luminescent converter for Si solar cells

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*Напівпровідникові сонячні елементи (вироблені з кремнію) мають різкий спад спектральної чутливості як в короткохвильовому так і в довгохвильовому діапазонах. Ефективне фотовольтаїчне перетворення з УФ і ближнього ІЧ діапазонів до видимої ділянки спектра є досить перспективним. В данній статті провадиться огляд основних можливостей створення такого люмінесцентного трансформтора. В спеціальному композиті екситони Френкеля утворюються при поглинанні світла та переносять енергію до молекулярних пасток, які випромінюють світло в області максимальної спектральної чутливості сонячного елемента.*

*Ключові слова: сонячний елемент, люмінесцентний трансформатор, спектральна чутливість.*

*Semiconductor solar cells (eg, silicon) have both rapid shortwave and longwave decrease in sensitive characteristics. Spectral response of mono-Si solar cell increases with wavelength in the range of 400-890 nm with maximum at 890 nm, beyond this maximum decreased rapidly and found minimum at the wavelengths less then 400 nm and more then 1100 nm.[3] That is why the realization of efficient UV-to-Vis and NIR-to-Vis conversion has a huge potential in photovoltaics. In practice, even 400 nm radiation does not allow efficient photovoltaic conversion. In order to fix this, it proposed to use luminescent converter. The possibilities of such converter design, based on dyes sensitized polymers are examined in this paper. For down conversion it is possible to make optically passive luminescent layer on the solar cell front surface. For the up-conversion the triplet-triplet annihilation process is possible at the back surface. Frenkel excitons, which are generated by the absorbed Solar light, transport excitation energy to molecular traps emitting light in the maximum spectral sensitivity of the solar cell in proposed luminescent converters or transformators. The introduction of the luminescent converter does not change the design of the solar cell, but it increases its spectral sensitivity, which makes this technology a promising direction for commercial application.*

*Key Words: solar cell, luminescent converter, spectral sensivity.*

Статтю представив член-кор. НАН України, д.ф.-м.н., проф. Макара В.А.

## Introduction

The solar cells efficiency highly depends on the band-gap of reactive semiconductor (for Si ~1.12 eV at room temperature). The Shockley–Queisser model states that semiconductor can't absorb photons of lower energy than band-gape. After absorption of high energy photons charges undergo thermalization.[1] For Si the Solar radiation with wavelength less than 400 nm is absorbed mostly in near surface layers. Due to the presence of the significant quantity of defects here the majority of charge carriers is captured by these defects and do not contribute in photocurrent.

Remaining 67% of incident solar energy at Earth surface (under AM1.5-G) not undergo photoviltaic conversion in Si SC. Solar spectrum with Si sensitive edges could be found on Fig.1.[2] This spectrum includes 39% in VIS, 52% NIR and 9% in UV range.

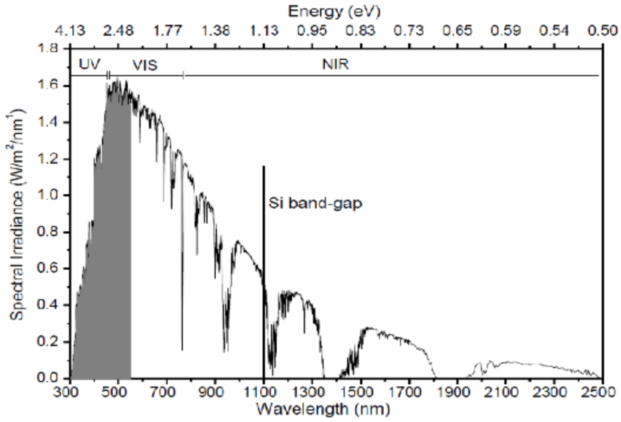

Fig.1. Sun spectrum at the Earth surface (AM 1.5-G) with short-wave edge and Si band-gap

Spectral response of mono-Si solar cell increases with wavelength in the range of 400-890 nm with maximum at 890 nm, beyond this maximum decreased rapidly and found minimum at the wavelengths 350 nm and 1100 nm.[3]. In practice, even 400 nm radiation does not allow efficient photovoltaic conversion. In order to fix this, it proposed to use luminescent converter. There are number requirements to this converter. First of all, the transparency in the range of the maximum spectral sensitivity of a silicon solar cell with absorption of the spectral range below 400 nm for shortwave and more than 1100 nm for longwave edge.

Problems in photoviltaic conversion that are caused mostly by thermalisation, transmition and fill factor losses in Si and other semiconductor material could be plotted as function of energy conversion efficiency (Fig.2.).

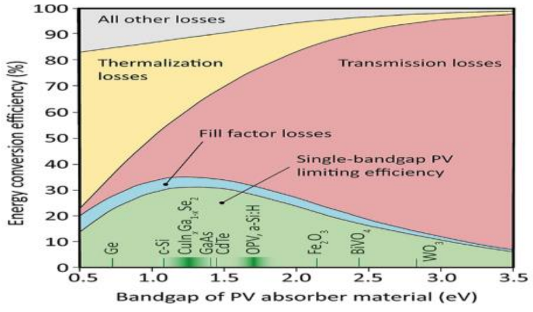

Fig.2. Fundamental loss mechanisms in solar energy conversion as a function of ther semiconductor bandgap for different materials (for 6000-K spectrum).[2]

As the down conversion coating will placed on the front of the photovoltaic device it must not interact with solar light in the range where it absorbed by solar cell. Also it needs to decrease loss of down-converted photons from the front surface of the coating[4]. Upconversion (UC) of low-energy photons (NIR) into light that can be utilized leads to increase of the efficiency of SC. The sensitized triplet–triplet annihilation-based upconversion (sTTA-UC) is the most perspective among UC mechanisms.[1]

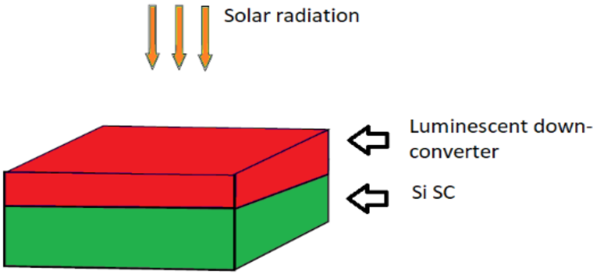

Fig.3. Down-converter deployment scheme

## Review of methods

As Si has two different edges of spectral sensitivity there are two groups of methods for it increasing. Down-conversion for high energy photons and up-conversion for low energy edge.

### 1.1 Down-conversion

To improve efficiency of Si SC down-conversion is a feasible way. Ideal down-converter is a 3-energy level system in which one photon with high energy is converted into few low energy photons. On practice some of high energy photons undergo intercombination transitions and do not give any contribution in sensitivity enhancement. Down-converter is a passive optical devise with linear optical processing, so it is possible to enhance efficiency using unconcentrated light and SC without modifications (Fig.3)[2].

There are 3 types of down-conversion devices, based on: organic luminescent dyes, semiconductor quantum dots (inorganic) and rare-earth ions (inorganic or organic complex).

### 1.1 Luminescent dyes

It was proposed to use a multi-component composite in transparrent matrix – Polystyrene (PS) or polyepoxypropilcarbazol (PEPC)[10]. F.Weigar found that in the anthracene crystal with an impurity of tetracene approximately 0.1-0.001% makes the spectrum of the fluorescence crystal coincides with that of tetracene, although all the exciting radiation absorbs anthracene[5]. For this reason it was decided to use anthracene and tetracene as a filler for the matrix with dyes such as Dicyanomethylene (DCM), Coumarin, Rhodamine6g, etc. Some authors propose to use polymethylmetacrylate (PMMA) as a matrix with the same dyes.[2].

### 1.2 Semiconductor quantum dots (QDs)

It have been successfully employed zinc-oxide and $TiO_2$ nanoparticles as luminescent down-shifting-layer (with possibility to use $Fe_2O_3$, $ZrO_2$, $Nb_2O_5$,

$Al_2O_3$, and $CeO_2$)[6]. Changing size of nanoparticles and using of multilayer system it is possible to get needed optical properties. Another material for down-converter is PbS, PbSe. For this QDs it is possible to tune emitted wavelength from 800 to 1800 nm, varying it size. They have extremely high quantum efficiency. QDs is very stable with excellent optical quality but they are very expensive. ZnO is a semiconductor with direct wide band-gap (Eg = 3.4 eV). Binding energy for exciton of ~60 meV makes it excellent candidate for stable luminescent conversion at room temperature.[2].

### 1.3 Rare-earth ions

It is used trivalent lanthanide ions in down-converter, but the width of it excitation band is not enough for commercial application. Some authors propose to use Er/Yb embedded Te Glass, Other propose heterostructure of $Y_2O_3$: [($Tb^{3+}$-$Yb^{3+}$), $Li^+$ ] quantum cutting with ZnSe that absorb incident light with energy higher than band-gap with further transfer to $Tb^{3+}$-$Yb^{3+}$. The result – conversion from a wide spectral range of 250-550 nm. Down-conversion is maximized by the energy match between ZnSe band-gap and Tb3+ absorption of 7 F6→5 D4.[1],[2],[7] The only one problem is a high price of such converter.

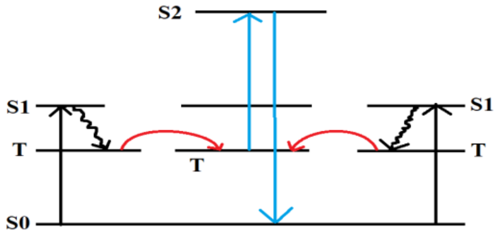

Fig.4. Energy diagram of sTTA-UC. Here describe process of light absorption with excitation of singlet states S1 of donor molecule, further intercombination transition to triplet state T with ET (red line) to acceptor in which undergo TTA.

### 2 Up-conversion

Among various ways of up-conversion of noncoherent solar radiation in photocatalytic devices the most recent and promissing is the Sensitized Triplet–Triplet Annihilation-Based Upconversion (sTTA-UC). TTA is a promising approach with low requirement to excitation light density with rather high quantum yield and tunability.

For STTA-UC energy transfer between donor (sensitizer) and an acceptor molecule (annihilator) is essential. STTA-UC is a multistep process involving energy transfer(ET) through metastable optically dark electronic states. Extra energy is given by ET from other ions or molecules (sensitizers) by annihilation after biexcitonic collisions. High energy photons emanates in radiative transfer from higher energy levels to the ground state.

One type of ions or molecules couldn’t provide us with all needed energy levels and one excite ion or molecule couldn’t absorb more than one photon which bring losses to intensity. Which is why EEET is frequently used. The energy-levels diagram of sTTA-UC is presented at Fig.4: Here sensitizer absorbing (αsens) photons and excites into Ss, undergoes through intersystem crossing (ISC) into the triplet state (ST). Then competes with back energy transfer (BET) to ET. ET can spontaneously decay (with a rate constant kSD) or undergo TTA to an excited singlet state of the emitter (ES)[2], [10].

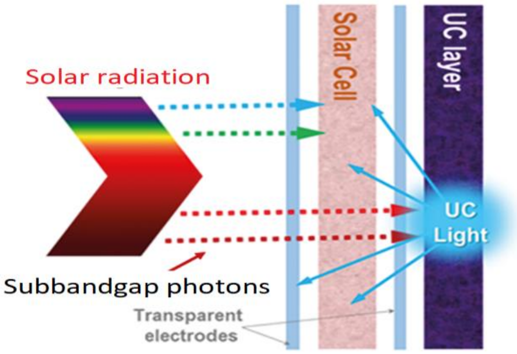

Fig.5. Deployment scheme of UC layer at the back of SC [2]

Si posseses IR transparent gap so sTTA-UC layer should be deployed on the back of SC and could be provided with reflector to enhance efficiency. [7],[8],[9]. With different materials UC efficiency is varied from 1.2 × 0‒3% to 12% (with C60). The scheme of UC deployment is described on Fig.5.

### Conclusion

At one hand down-converter is a passive optical device and Si is transparent in IR, so it is possible to put down-converter on the front of SC with UC at the back side. Such deployment may significantly increase efficiency of photovoltaic conversion. At another hand efficiency of light conversion and limited list of materials for conversion is an actually problem for commercial use of this technology. The most novel and advanced problems are searching for new NIR-to-vis material, reducing of reflection losses and enhancing of efficiency of UC mechanisms. Obtained results indicate that the application of TTA-UC to comercial devices demands the realization of stable integrated materials e.g. by embedding the upconverter structure in transparent matrices. Results of this review will lead to luminescent converter design at Faculty of Physics, T.Shevchenko National University of Kyiv in cooperate with V.Ye. Lashkaryov Institute of Semiconductor Physics (ISP), NAS of Ukraine, Institute of organic chemistry NAS of Ukraine.

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