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Zinc oxide nanoparticles for improvement of thin film photovoltaic structures' efficiency through down shifting conversion

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ABSTRACT

The paper presents the idea to improve the performance of thin film photovoltaic cells by a light capture enhancement through the introduction of down shifting energy converters. Luminescent down shifting layers convert high-energy photons (UV light) into low-energy ones (visible light), which are more efficient in a photovoltaic conversion. For this purpose, the application of a thin layer composed of zinc oxide (ZnO) nanoparticles deposited onto a thin film solar cell is proposed. The paper presents both experimental and theoretical results of this approach. Conducted investigations include an analysis of ZnO nanoparticle layers, deposited in two independent technology methods. The results showed that ZnO nanoparticles have a great potential of application as down converting layers and can be implemented to improve the efficiency of photovoltaic cells, especially in the field of thin film PV structures. The proposed new deposition method can potentially be used in some industrial photovoltaic applications.

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1. Introduction

The maximum theoretical efficiency of a single junction solar cell is referred as the Shockley–Queisser limit [1] and mainly depends on the matching between the solar emission spectrum and the absorption spectrum of a solar cell active layer material. The maximum photovoltaic efficiency value of a solar cell is determined by such parameters as: optical absorption coefficient of the material, surface reflection, carrier transport and carrier collection [2]. Other factors, contributing to the limitation of the PV conversion efficiency in a single junction solar cell are related to the fact that only a part of the solar emission spectrum is absorbed in the photovoltaic device. The semiconductor layer is transparent to the photons of energy below the bandgap, but the thermalization of charge carriers generated by high-energy photons absorption is one of the major loss mechanisms by which collected solar energy is underutilized in conventional solar cells [3]. A large number of approaches can be used to surpass this photovoltaic conversion efficiency limit. One can point out such solutions as: development of tandem solar cells, optical excitation through midgap defect levels allowing utilization of low energy photons, methods employing

capturing of infrared light and hot electrons or multiple electron generation, fluorescent down-conversion or thermophotovoltaic down-conversion [3–7]. The method proposed in this paper for reducing these energy losses and enhancing the conversion efficiency of solar cells is based on the down-shifting (DS) concept.

In general, the research on luminescence down-shifting has been aimed at converting the shorter wavelengths to longer ones [3]. The possibility of down-conversion, in order to enhance solar cells' performance has been investigated theoretically by Trupke et al. [8]. The luminescence converter is located on the front surface of a solar cell manufactured from a material with the bandgap energy E_g . The solar cell and the luminescence converter are assumed to have equal refractive indices. High-energy photons with $\hbar\omega > 2E_g$ are absorbed by the converter and efficiently down converted into two lower energy photons with $\hbar\omega > E_g$, which can be absorbed by the PV cell. The cell and the converter are electronically isolated from each other and a perfect mirror is located on the rear surface of the system [8].

The application of down converting and down shifting layers in PV includes luminescent solar concentrators [9–11] and measures to overcome limitations in the front surface of some solar cell designs [12]. For example, the luminescent silicon nanoparticle/polymer composite films that provided UV wavelength to visible light down conversion were proposed by Nayfeh [13]. Other methods for light trapping use the phenomenon of localized surface

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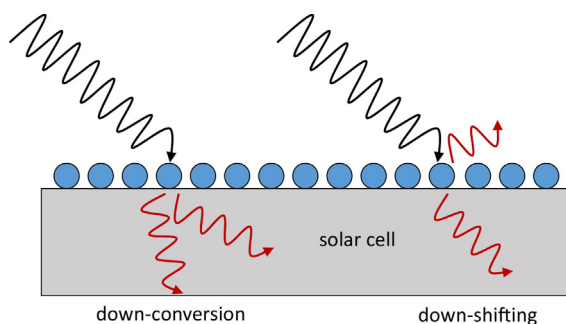


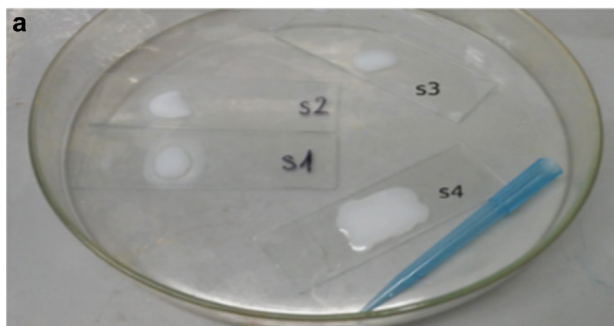
Fig. 1. Schematic illustration of the energy down-conversion and down-shifting concept, using nanoparticles as front layer of a solar cell, based on Ref. [2].

plasmon excitation in metallic nanoparticles, which are deposited on a semiconductor's surface. Pillai et al. [14] showed that silver nanoparticles deposited onto the surface of a single junction silicon solar cell can slightly enhance the light absorption and hence increase the photocurrent generation in the active silicon layer. On the other hand, Richards [11] reported a proposal of rare-earth-doped luminescent materials in this application. Unfortunately, he has not observed the significant benefits of using those materials for photovoltaic devices performance.

2. Approach

The basic idea of proposed approach for the improvement of solar cells efficiency is to apply the zinc oxide (ZnO) nanoparticle layers in the role of a down-shifting energy converter, at the front surface of a thin film solar cell. The novelty of this solution consists of the application of ZnO NP films as luminescent down-shifting layers. General concept of down-conversion and down-shifting using nanoparticles, is shown in Fig. 1.

Zinc oxide has recently aroused a considerable interest because of its advantageous optical and electrical properties, as well as possible multiple applications in photoelectrical and optoelectronic devices (such as piezoelectric transducers, optical waveguides, surface acoustic wave devices, varistors, phosphors, transparent conductive oxides, chemical and gas sensors, spin functional devices, and UV-light emitters [15–17]). The attractiveness of this wide bandgap semiconductor (3.37 eV at room temperature, corresponding to an absorption wavelength of 375 nm) is also growing because it is a non-toxic, inexpensive and abundant material, characterized by much simpler crystal-growth technology than other wide bandgap semiconducting materials. Because of its wide bandgap, ZnO is a promising material for photonic applications in the UV or blue spectral range, while the high exciton-binding energy (of 60 meV [15]) allows for an efficient excitonic emission even at room temperature.



Conducted investigations showed that ZnO nanoparticles have a great potential of application as down converting layers. ZnO nanoparticle films were fabricated using two independent methods. The first one is an original and purely physical method, which is performed in the gas phase, called: Low Energy Cluster Beam Deposition (LECBD). The method was described by authors in more details elsewhere [18]. The stoichiometry, crystallinity and surface quality of the obtained layer can be adjusted via control of the LE CBD synthesis parameters. The process of obtaining ZnO NPs includes the following steps. A cluster generator based on a combined Nd:YAG laser vaporization and a rare gas (Ar) condensation source is used to deliver a supersonic jet of nanoparticles with sizes ranging from a few tens to some thousands of atoms (diameters varying from 2 to a few nm). A stoichiometric ZnO powder (99.99% pure) that was pressed and heated in a furnace at high temperature under oxygen atmosphere is used as the target. The oxygen is injected in the argon flux present in the nucleation chamber. Different values of the oxygen partial pressure as compared to the Ar pressure are applied in order to obtain the ZnO NPs with diverse stoichiometry. The deposited ZnO NPs assembly has the same stoichiometry as the plasma. The nucleation process occurs in a supersonic nozzle, where atoms are hyper-quenched beyond the thermodynamic equilibrium [19]. The second method is chemical and it uses ZnO nanoparticles dispersed in the polymer matrices. Such compositions were deposited on the surface of the substrate in spin coating technology, with adequately and carefully selected parameters of the process. Fig. 2 presents various types of the prepared compositions (a) and a glass sample after spin coating deposition process inside the deposition equipment (b).

Compositions shown in Fig. 2(a) are all solutions of ZnO nanoparticles in water–polymer solvents. Samples vary in water:polymer solvents' proportions, which are the following:

-) s1 – 1:1,
-) s2 – 2:1,
-) s3 – 3:1,
-) s4 – 4:1.

Concentration of ZnO nanoparticles in all samples is 15 mg/mL of a solvent. Before deposition all glass substrates have been cleaned using methanol and deionized water. Spin coating deposition process was realized according to the following parameters: velocity of 200 rpm (rounds per minute), with the initial acceleration of 20 rpm/s and deposition time equal to 30 s.

3. Results, analysis and discussion

Basing on the experiments with ZnO NP layers' deposition, their implementation in photovoltaic structure has been proposed. As an initial step, a standard silicon PV cell, with ZnO NP layer deposited in LE CBD technology, was prepared. Current–voltage characteristics

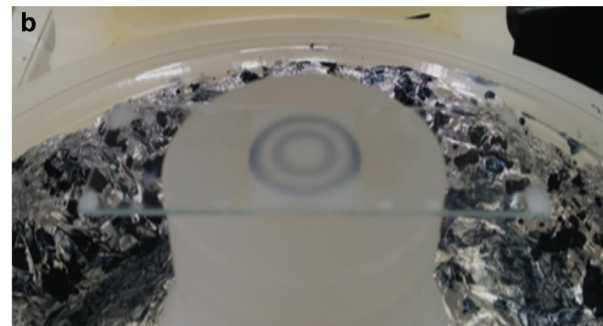


Fig. 2. Compositions prepared using ZnO nanoparticles (a) and a glass sample (b) with ZnO NP layer deposited in spin coating technique.

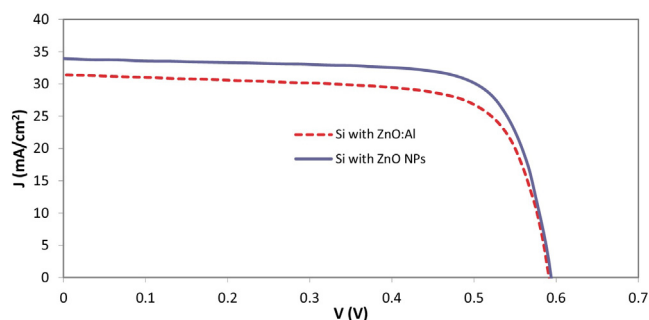


Fig. 3. J-V characteristics of prototype silicon solar cells equipped with a transparent conductive layer based on ZnO:Al and photoluminescent ZnO NPs layer.

confirmed the superiority of cells with photoluminescent layers over structures with passive ZnO filter, which is shown in Fig. 3.

The influence of a down shifting ZnO nanoparticle layer on the performances of thin film photovoltaic structures was also determined. For that purpose, a series of computer simulations using the SCAPS (Solar Cell Capacitance Simulator) software has been conducted. These simulations have been based on the numerical models, that were created taking into account the real construction and thus optical and electrical properties of each layer of the structure. During the simulations, material and electrical parameters of the cell have been adjusted according to the experimental results and work configuration. For this goal ZnO NPs luminescence spectrum, measured by the photoluminescence excitation method has been incorporated into the AM 1.5G illumination curve in order to model the performances of thin film PV cells equipped with a top ZnO NPs luminescence layer. Computer simulation results performed by authors in such mode were presented for CIGS and CdTe thin film photovoltaic structures in Ref. [20].

The J-V characteristics calculated numerically for two different types of thin-film photovoltaic structures, with and without the ZnO NPs layer, confirm the large potential of the proposed solution of down-shifting energy converters in the thin film solar cells design. Their implementation in the PV structure improves the photocurrent and thus the global efficiency of the device. Obtained results indicated the efficiency gain up to 15% due to implementation of ZnO NPs layer instead of standard ZnO:Al emitter contact in CdS/CdTe structure and close to 6% in CIGS constructions.

Further step in the development of the proposed down-shifting solution was to transfer the idea of ZnO NP layers into easier and more available technology method. For that purpose, a set of samples of ZnO nanoparticles dispersed in polymer matrices, was prepared. Compositions containing ZnO NPs of approximately 20 nm diameters were deposited on quartz glass using spin coating technique. Fig. 4 presents the picture of used nanoparticles obtained with scanning electron microscope representation.

Results of the excitation and emission spectrum for an example sample deposited on a glass substrate are presented in Fig. 5. It shows that the layer and the material responsible for the emission absorbs the irradiation from the range between 280 and 400 nm. The emission for ZnO nanoparticles which was excited by such wavelengths is considerably visible, which proves the possibility of preparing the proper suspension of ZnO NPs in polymer matrix, as well as its potential application as down shifting material for the improvement of solar cells efficiency. These results show the validity of the chosen direction of research with the indication of their further development.

The compositions for spin coating deposition technique are still in the phase of elaboration and improvement. Currently authors are working on increasing the amount of ZnO nanoparticles in developed solutions.

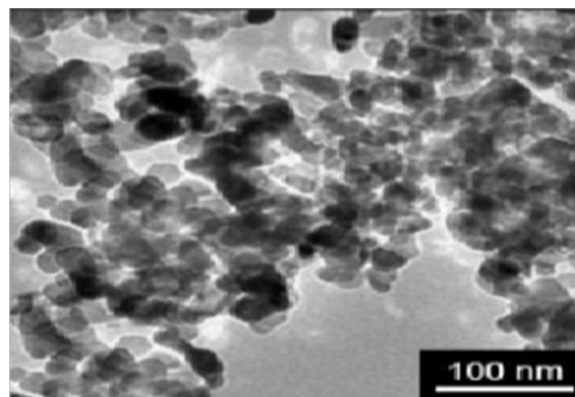


Fig. 4. SEM picture showing ZnO nanoparticles used in composition deposited on glass substrates.

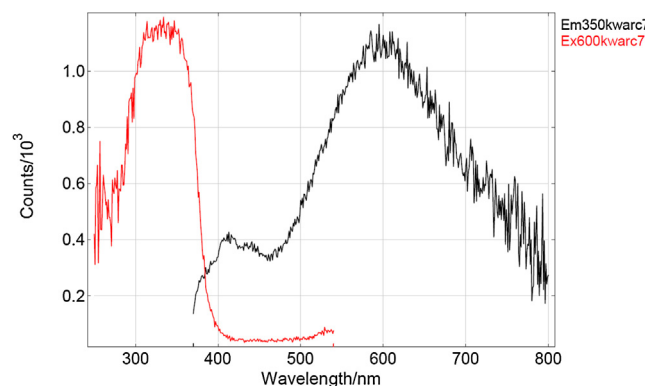


Fig. 5. Excitation (red) and emission (black) spectrum curves of ZnO nanoparticle layers (with ZnO NP size of 20 nm) deposited on quartz glass using spin coating technique.

4. Conclusions and perspectives

Concluding from the practical experiments and computer simulations performed with the SCAPS program, the presence of the luminescent ZnO NPs down-shifting layer on the top of a solar cell structure has an influence on its optoelectronic performance. Both measured J-V characteristics of a silicon solar cell and those simulated of thin film PV structures, are strongly affected by the presence of the photoluminescent ZnO NPs down-shifting layer on their top. The modification of the AM 1.5G solar emission spectrum by a luminescent emission of the investigated material permits to put in evidence the improvement in the shape of the J-V characteristics, as well as of increase of the PV cell final efficiency. Obtained simulation results indicated efficiency gain of 15% due to implementation of ZnO NPs layer in CdTe/CdS photovoltaic structure. This leads to the conclusion that even a slight increment of the quantity of incident light hitting the solar cell is falling into the spectral absorption domain of the active material which increases the quantity of the photogenerated carriers and thus the overall efficiency of the solar cell.

Taking the advantage of the promising studies, further step was to develop a novel technology of a zinc oxide nanoparticle layers' deposition on thin film photovoltaic cells, which can be easily implemented at the industrial level. For this purpose, as an initial one, spin coating technology was proposed and compositions containing ZnO nanoparticles in polymer matrices were developed. Those ZnO NPs, being embedded in a transparent layer on the top of the solar cell structure, would play the role of effective energy down-converters increasing its efficiency.

Further development and improvement of the deposition method, as well as compositions' preparation process, are concerned to provide industrial application of the proposed solution. Next step which is planned to be realized within the proposed approach will be experimental evaluation of CdTe/CdS solar cells with ZnO NPs.

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