



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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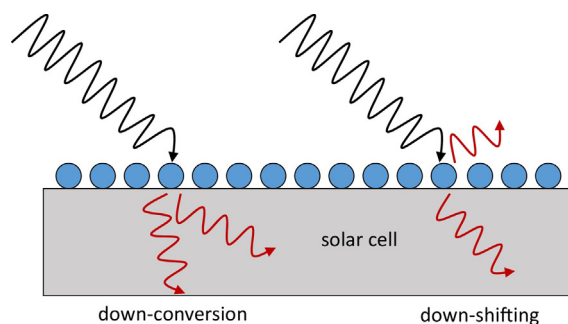


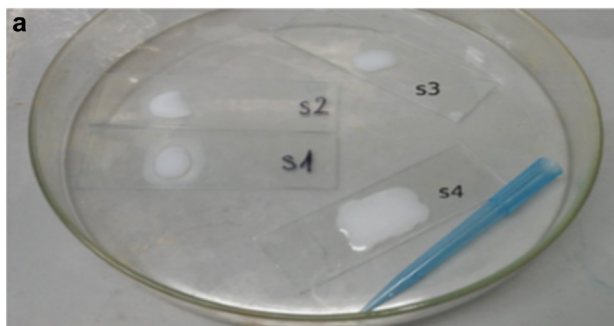
Fig. 1. Schematic illustration of the energy down-conversion and down-shifting concept, using nanoparticles as front layer of a solar cell, based on Ref. [2].

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

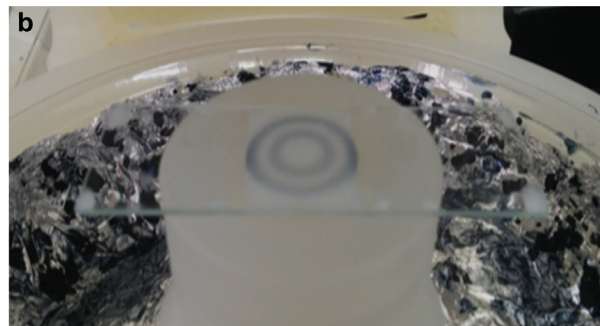


Fig. 2. Compositions prepared using ZnO nanoparticles (a) and a glass sample (b) with ZnO NP layer deposited in spin coating technique.

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