Natalia Szczecińska, Katarzyna Znajdek, Aleksandra Sosna-Głębska, Paul Lewicki, Przemysław Czarnecki, Piotr Kraska, Cezary Bazdyga
Department of Semiconductor and Optoelectronics Devices, Faculty of Electrical, Electronic, Computer and Control Engineering, Lodz University of Technology
Wólczańska 211/215, 90-924 Lodz, Poland, nataliaszczecinska@o2.pl

Gabriela Wiosna-Sałyga
Department of Molecular Physics, Faculty of Chemistry, Lodz University of Technology,
Żeromskiego 116, 90-924 Lodz, Poland

Maciej Sibiński
Department of Semiconductor and Optoelectronics Devices, Faculty of Electrical, Electronic, Computer and Control Engineering, Lodz University of Technology
Wólczańska 211/215, 90-924 Lodz, Poland

THE PHOTOLUMINESCENT LAYERS BASED ON ZnO NANOPARTICLES AS RADIATION CONVERTERS IN PHOTOVOLTAIC APPLICATIONS

Abstract
The mismatch between solar cell response and solar spectrum is one of the biggest challenges to achieve high efficiency in photovoltaic cells. There are a few different approaches to minimise this concern. One of them is the radiation conversion which may be due to three different processes, namely up-conversion, down-conversion and down-shifting. In this paper the down-conversion process of zinc oxide nanoparticles (ZnO NPs) and layers with ZnO NPs in polymer (poly (methyl methacrylate)) (PMMA) matrix will be analysed. ZnO NPs are prone to act as down-converting or down-shifting agents, which absorb the UV radiation, which is not absorbed by the solar cell, and then re-emit light in the visible range, which is suited to the photovoltaic cell sensitivity. Herein, the photoluminescence and optical transmittance of ZnO NPs and layers based on ZnO NPs will be presented. These parameters have a large influence on the potential application of these layers in photovoltaic structures for increased efficiency. The conversion layers have to fulfil the following conditions: have good optical transmittance in the visible range and high luminescence efficiency in converting UV radiation into visible. The paper focuses on finding the balance between these parameters.

Key words
down-conversion layers, down-shifting layers, photoluminescence nanoparticles, solar cell efficiency, zinc oxide nanoparticles, photoluminescence layers

Introduction
The photoluminescence effect has a wide spectrum of applications in many different domains of industry [1-3]. In photovoltaics it is used in the non-destructive quality control of solar cells [3, 4], the luminescent solar concentrator [5] and radiation converters [6, 7]. Fundamental spectral losses arising from the limited spectral response of solar cells to the solar radiation spectrum create the greatest part of the deficiency of photovoltaic devices. These losses limit the theoretical maximum efficiency of a single junction solar cell with an energy band-gap of E_g = 1.1 eV (c-Si cell) to a mere 31% [8]. During the last few decades various concepts have been proposed to overcome that limit such as multi-junction solar cells, interband transitions or radiation conversion methods [9-11].

The three fundamental radiation conversion processes: up-conversion (UC), down-conversion (DC) and down-shifting (DS) are schematically presented in Fig. 1. The first process permits the conversion of infrared light into visible light by the simultaneous absorption of two photons and emission of one photon with higher energy. In the down-conversion process one photon with higher energy can be converted into two photons of equal energy, two times less than the one absorbed. The last one (down-shifting process) is a variant of the down-conversion technique, which permits the conversion of a high-energy photon into lower-energy photons [6, 7, 10, 11].

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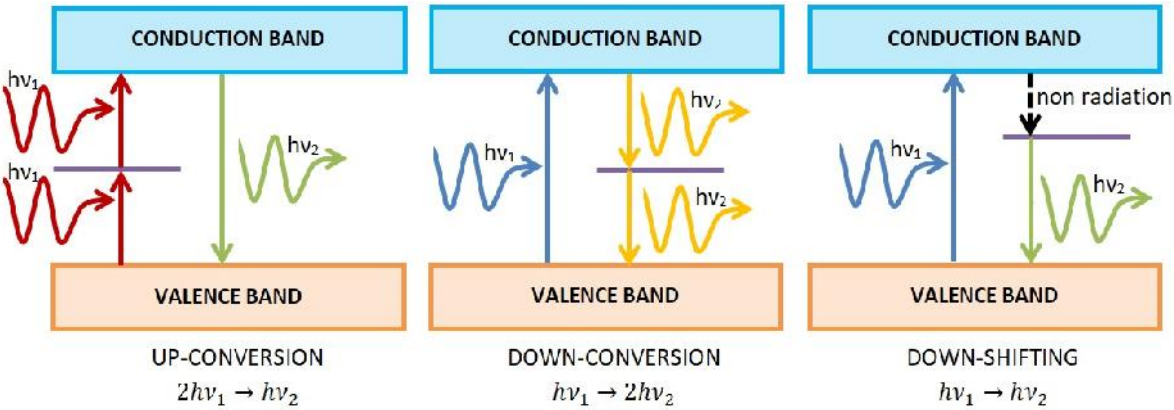


Fig. 1. Schematic of the converting processes: up-conversion, down-conversion and down-shifting.
Source: Authors

The use of down-conversion to improve solar cell efficiency was first investigated by Dexter [12]. More than 20 years later, Hovel et al. [9] proposed down-shifting, a similar process. During the last few decades various materials were examined for application of the down-conversion or down-shifting process [13, 14]. Abrams et al. [10] and Trupke et al. [11] calculated the increase of a conventional single-junction solar cell efficiency equal to 7% as a result of the application of a down-converting layer. A similar conclusion was reached by Gabr et al. [15]. The enhancement of solar cell efficiency with the application of down-converting layers incorporating rare earth (RE) elements [16-18], quantum dots [19-22] and others [6, 13, 14, 23] has been observed. For example the influence of conversion layers based on RE at solar cell efficiency was studied for dye-sensitized solar cell (DSSC) using ZnO doped various RE where the rise of efficiency is about 2% [17]. The similar rise was observed for the same type of solar cell using SrAl2O4 with Eu and Dy [18]. The application of CdS QDs as converters in GaAS solar cells causes the increase of efficiency for about 3% [22]. ZnO NPs was analysed in [6] where the growth of efficiency was observed for CIGS and CdTe solar cells for almost 1% absolutely what give the relatively rise for about 5%.

The results of a computer simulation of zinc oxide nanoparticles (ZnO NPs) using SCAPS (Solar Cell Capacitance Simulator) software suggested a possible increase of solar cell efficiency of about 2% to 3% for different photovoltaic structures: traditional polycrystalline silicon (poly-Si), cadmium telluride (CdTe) and copper indium gallium selenide (CIGS) solar cells. The higher influence of the layers was observed for CdTe solar cell [24]. The photoluminescence properties and optical transmittance change (due to the refraction coefficient change) have the main influence on that. In this paper the properties of manufactured down-converting layers based on ZnO NPs are analysed and discussed.

Zinc oxide (ZnO) is a direct bandgap semiconductor with great potential for a variety of applications. A wide bandgap of 3.37 eV achieved at room temperature [23] makes ZnO a promising material for optoelectronic and photonic applications in the UV or blue wavelength spectral range. At the same time, the high exciton binding energy ensures an efficient exciton emission even at room temperature. Furthermore, ZnO has many advantages. It is cheap, abundant and an environmentally friendly material which exhibits a visible emission related to crystal defects, suitable for down-shifting [23]. Also, its semiconducting properties make ZnO sensitive to the doping process. One of the most popular doped material is aluminium (Al) which creates an aluminium-doped zinc oxide (AZO). The AZO is a highly conductive n-type material. The doping of ZnO also influences its optical properties [25, 26] which can be used to tune the emission colours.

Materials and Methods

The down-conversion layer was deposited by spin-coating methods at various spin speeds of: 1000 rpm, 2000 rpm, 3000 rpm, 4000 rpm, 5000 rpm and 6000 rpm. The layer's matrix is a poly (methyl methacrylate) (PMMA) compound with an average molecular weight of 350000 by GPC, purchased from Sigma Aldrich Company. The material used to convert the UV radiation to visible range is ZnO NPs, purchased from IoLiTec Company (Ionic Liquids Technologies). The average ZnO NPs size is 20 nm. The solvent used was chlorobenzene.

The mixtures were prepared with different mass concentrations of ZnO NPs: 1%, 2% and 5%. Firstly, the ZnO NPs, PMMA and chlorobenzene were weighted. The mass concentration of the PMMA was 8% in the base matrix. Subsequently the mixtures were put in an ultrasonic cleaner for 30 minutes. In this way, the ZnO NPs are distributed in smaller agglomerates and are homogeneously distributed in the layer. Consequently, the samples were stirred with a magnetic stirrer for 24 hours under hermetic cover. Just before the deposition of the DC layer the mixtures were put into the ultrasonic cleaner for 30 minutes once again. In this case two kinds of substrates were used: quartz and silicon for optical transmittance measurements, photoluminescence measurements and scanning electron microscope (SEM).

The photoluminescence properties of the manufactured ZnO NPs layers were measured using an FLS980 (Edinburgh Instruments) fluorescence spectrometer with a 450 W excitation source ozone free Xenon Arc Lamp and R-928 photomultiplier detector. The optical transmittance was measured with a Filmetrics aRTie-UV LS-DT2. The SEM analysis was made with a Carl Zeiss EVO MA10 SEM scanning electron microscope using two detectors: SE for analysing secondary electron image and BSD for analysing backscattered electron image.

Results and Discussions

The optical properties of the DC layers were analysed. Considering the results of computer simulation [24], the optical transmittance should be as high as possible. When it is less than 85% the DC layer will not enhance the solar cell efficiency. This is caused by the fact that the layer absorbs the radiation, also from the visible range, which is used in photoconversion process in the solar cell. In Figs. 2-4 the characteristics of optical transmittance for the DC layer with different concentrations of ZnO NPs are presented. The line of 85% optical transmittance is marked in all figures. This level is exceeded for DC layers with ZnO NPs in concentrations of 1% and 2% for all spin speeds for wavelengths below 400 nm. Although the level of 85% optical transmittance for the DC layer with 5% ZnO NPs concentration is achieved with a spin speed of 1000 rpm at a wavelength of 540 nm. With a spin speed of 4000 rpm and more it is exceeded at a wavelength of 430 nm. High optical transmittance in the visible range is so important due to the effectiveness of utilisation of this radiation by solar cells. Moreover, the optical transmittance for 4000 rpm spin speed and higher is similar to each other for all concentrations of ZnO NPs.

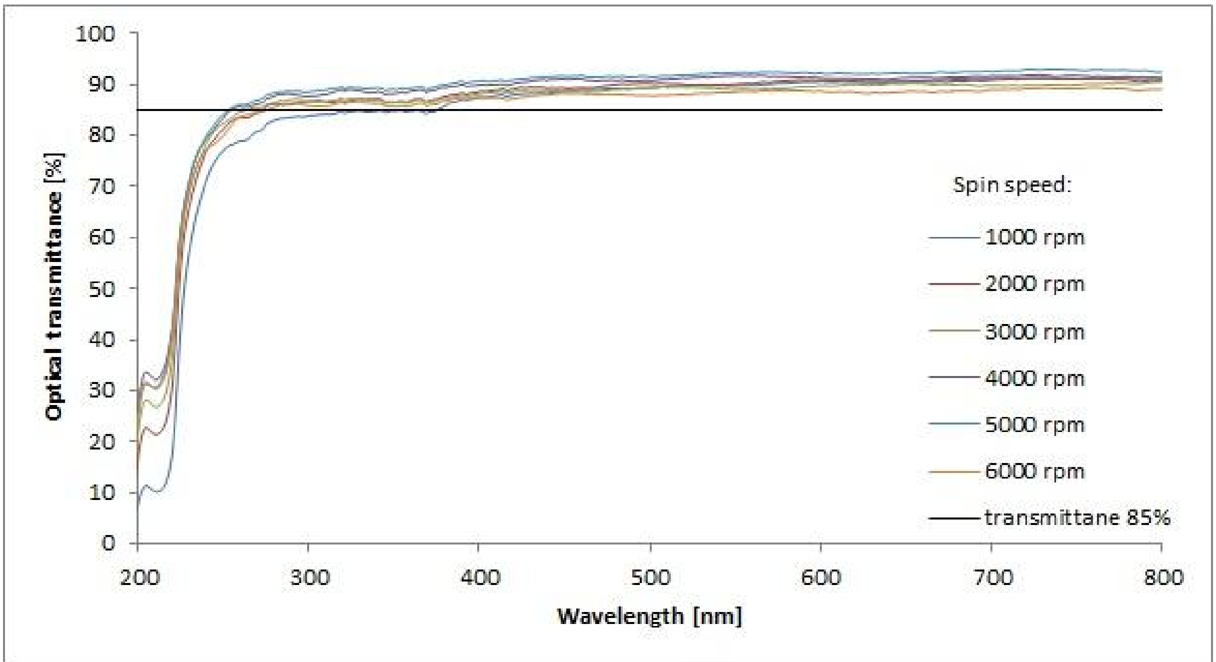


Fig. 2. Optical transmittance of down-conversion layer with ZnO NPs of 1% concentration.

Source: Authors

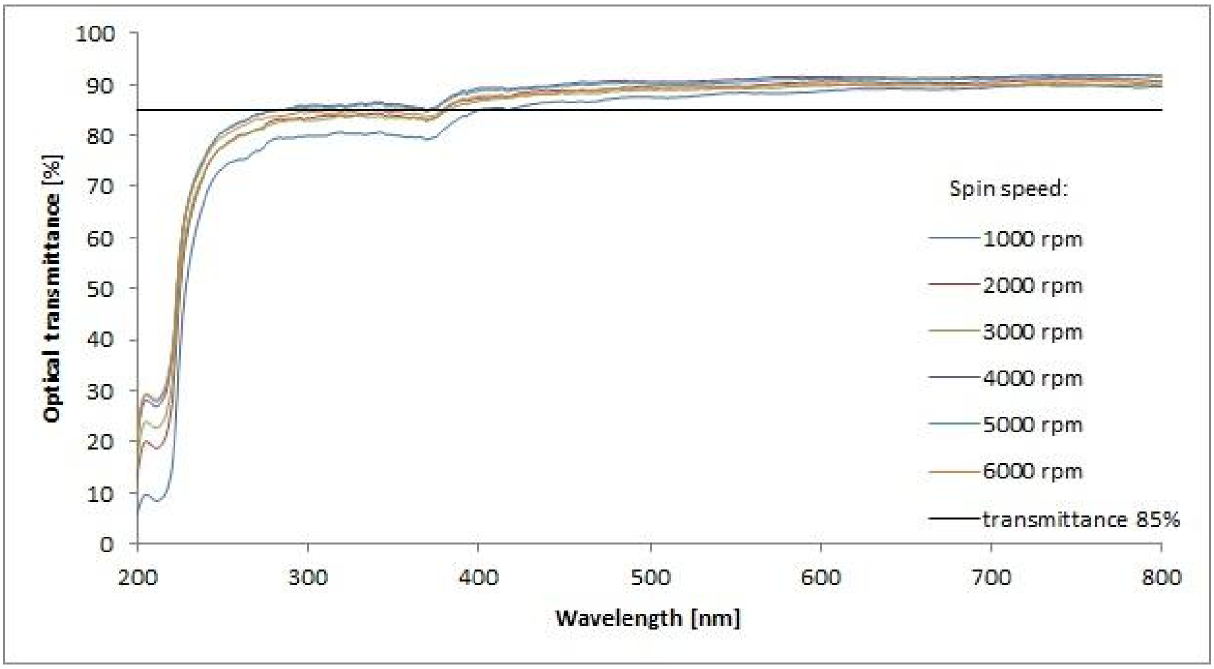


Fig. 3. Optical transmittance of down-conversion layer with ZnO NPs of 2% concentration.
Source: Authors

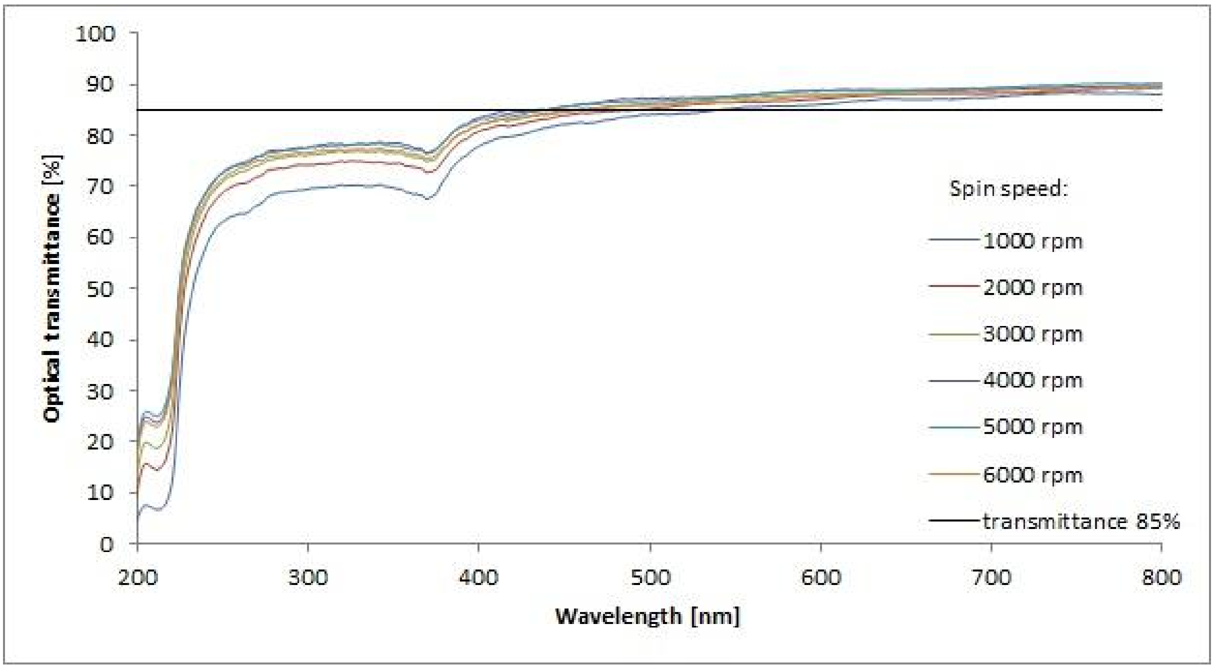


Fig. 4. Optical transmittance of down-conversion layer with ZnO NPs of 5% concentration.
Source: Authors

Fig. 5 presents the emission spectrum of zinc oxide nanoparticles in powder for various excitation wavelengths. The results show that examined ZnO nanoparticles have desirable photoluminescence properties to convert UV radiation into visible light.

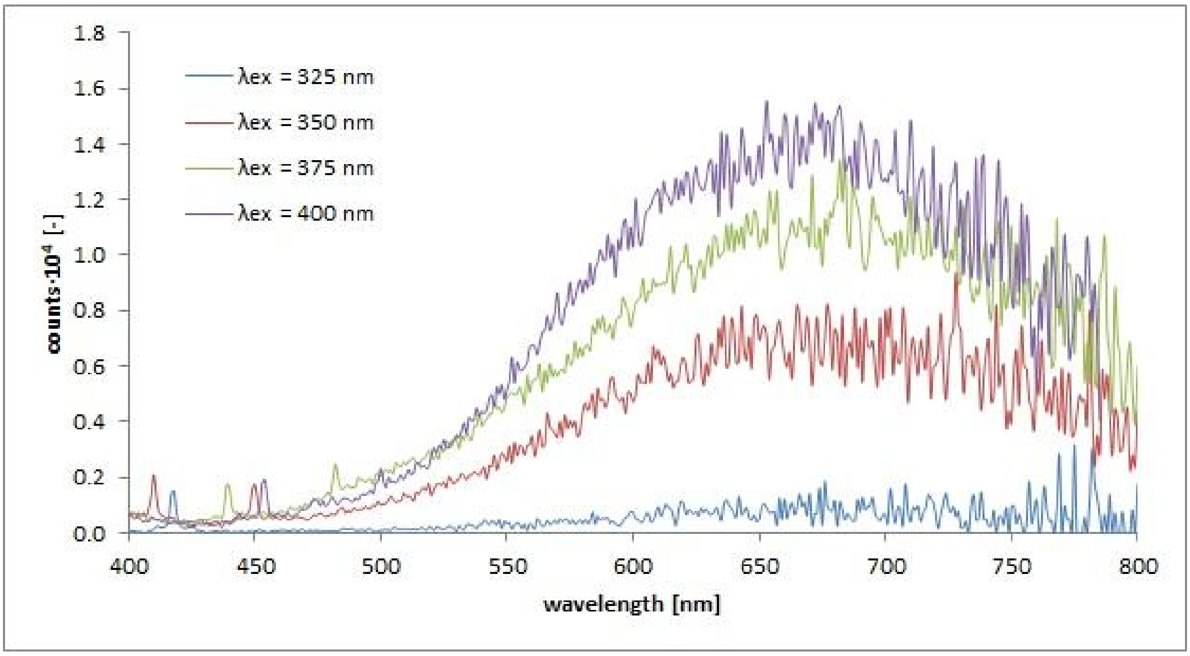


Fig. 5. The emission spectra of ZnO nanoparticles for various excitation wavelengths.
Source: Authors

The analysis of photoluminescence characteristics of ZnO NPs, and the results of computer simulation suggest that the optical transmittance for wavelengths above 430 nm should be as high as possible. For practical reasons, the authors considered application of the DC layer on the industrial type of thin-film, flexible solar cell. In Fig. 6 the external quantum efficiency of amorphous silicon (a-Si) of a solar cell by PowerFilm series MP3-37 is presented with optical transmittance of the layers obtained with spin speed of 4000 rpm and emission and excitation spectra of ZnO NPs. The emission excitation spectrum of ZnO NPs, which can be treated with some assumptions as absorption spectrum, matches the a-Si solar cell external quantum efficiency characteristic, as the solar cell is not sensitive in this range. The ZnO powder absorbs in the range of wavelengths 350-450 nm, in which the EQE for a-Si solar cell is low. Although the maximum of emission for ZnO NPs is shifted towards longer wavelengths, the value of external quantum efficiency of a-Si solar cell still exceeds 50% in this range, hence a DC layer based on ZnO NPs will potentially improve the efficiency of a-Si solar cell. The optical transmittance of all layers is more than 85% for the whole visible range.

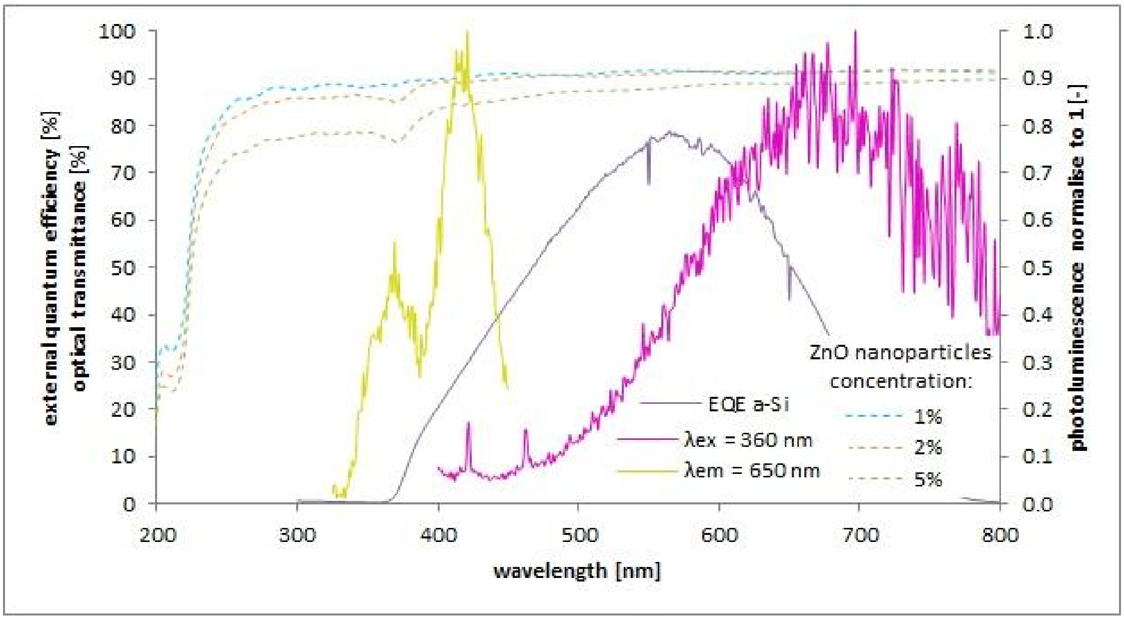


Fig. 6. The EQE of a-Si solar cell, the excitation end emission spectrum of ZnO NPs and optical transmittance of a layer with ZnO NPs in various concentrations for 4000 rpm spin speed .
Source: Authors

The emission spectra of DC layers with ZnO NPs are presented in Figs. 7-10 for various concentrations of ZnO. Interestingly, in the case of layers, intense blue emission is observed. The origin of the emission peak in the range of 400-470 nm is not completely understood. However it could be interpreted as emission coming from Zn interstitials states which are responsible for characteristic near-band-edge emission [27].

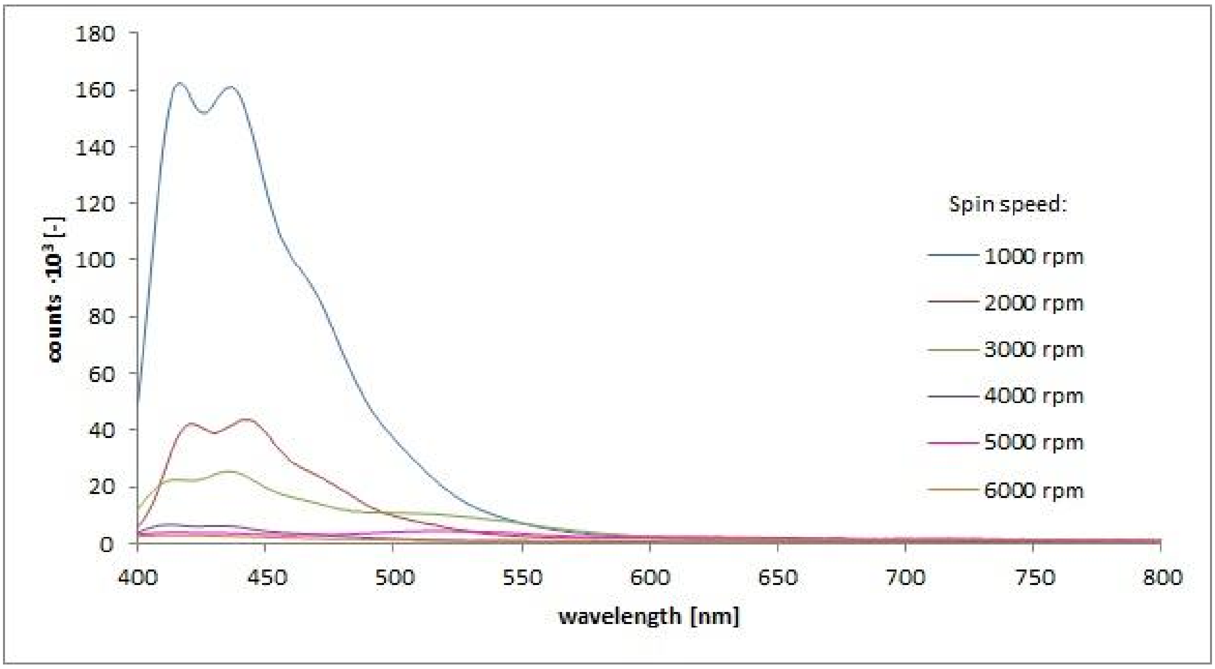


Fig. 7. The emission spectrum of down-conversion layer with ZnO NPs in 1% concentration.
Source: Authors

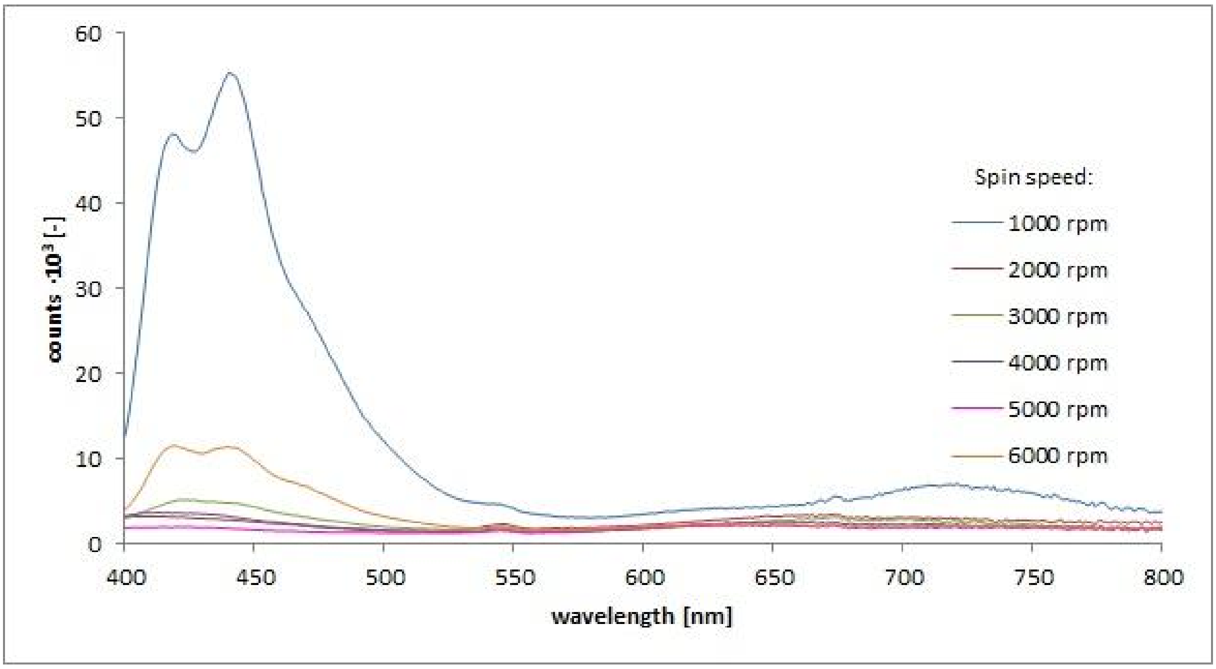


Fig. 8. The emission spectrum of down-conversion layer with ZnO NPs in 2% concentration.
Source: Authors

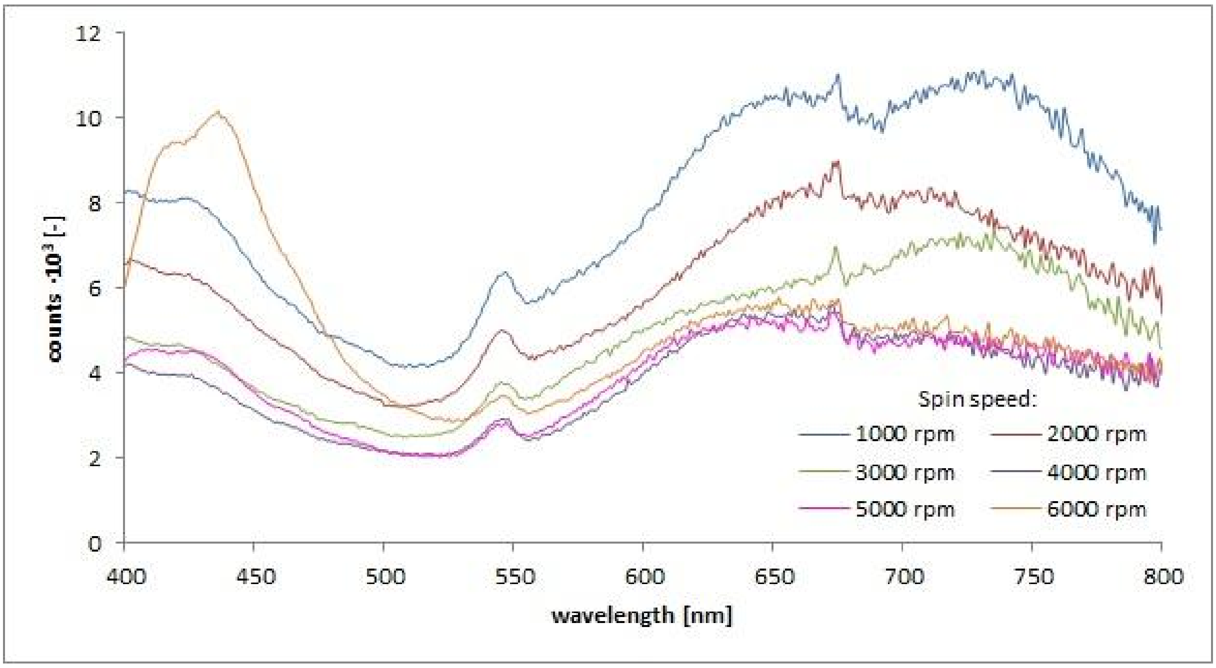


Fig. 9. The emission spectrum of down-conversion layer with ZnO NPs in 5% concentration.
Source: Authors

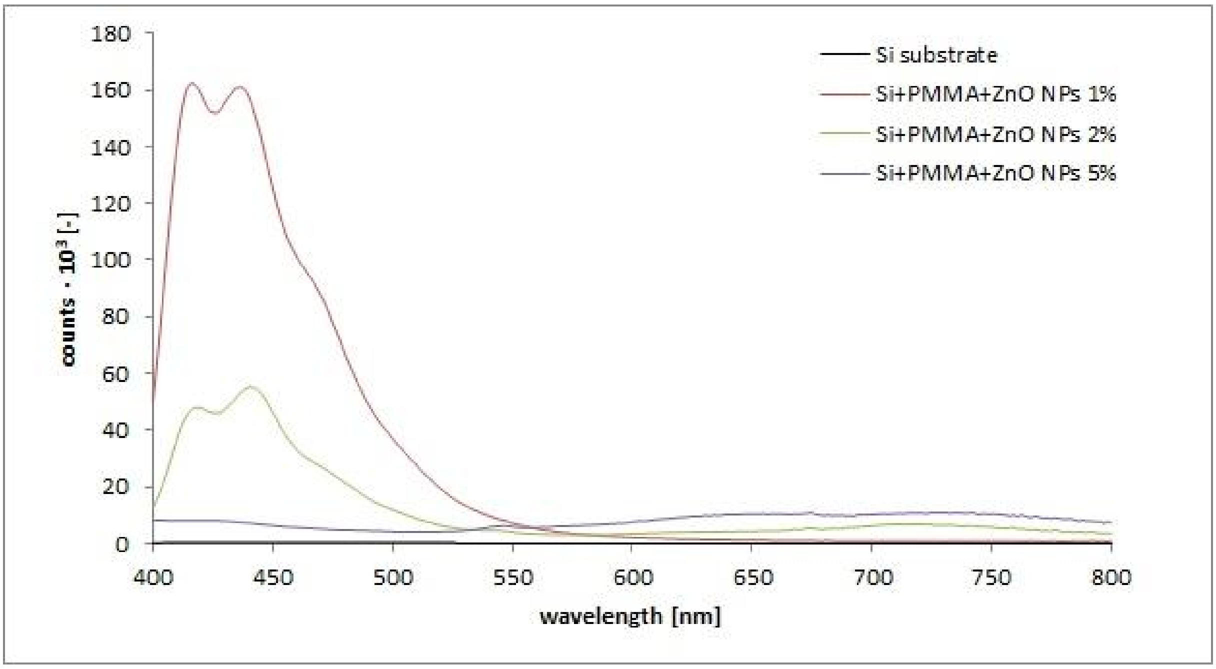


Fig. 10. The emission spectrum down-conversion layer with ZnO NPs of concentrations of 1%, 2% and 5% deposited at a spin speed of 1000 rpm.
Source: Authors

The results of optical transmittance and photoluminescence of DC layers with ZnO NPs in various concentrations suggested one of two different directions. The optical transmittance of the DC layer increases when the ZnO NPs concentration drops and the spin speed becomes higher. On the other hand, the emission spectrum of the DC layer is better with increased concentrations of ZnO NP and decreased spin speed. To meet the requirements for possibly high transmittance and high emission of the DC layer in the visible range, a compromise is needed. The golden mean seems to be a DC layer with 5% concentration of ZnO NPs fabricated at a spin speed of 3000 rpm (Fig. 11).

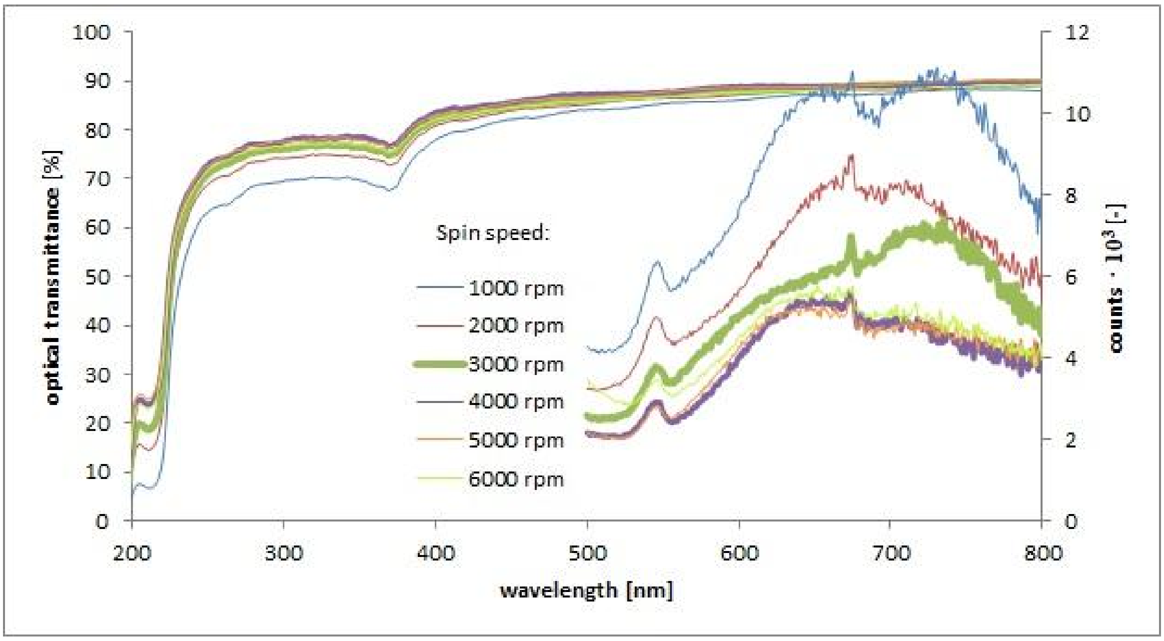


Fig. 11. The optical transmittance and emission spectra of down-conversion layer with ZnO NPs in the concentration 5% at a spin speed of 3000 rpm.
Source: Authors

The secondary electron image made with SEM for DC layers containing ZnO NPs in various concentrations are presented in Fig. 12. It can be seen that the morphology of the layers is similar and unrelated to concentrations of ZnO NPs. In Fig. 12d the exemplary surface profile is shown. It can be noticed that the surface of the DC layer is quite rough. Moreover, the SEM pictures show that ZnO NPs are grouped in small agglomerates, which are homogeneously distributed in the layer. The homogenous layer has more uniform parameters and will have an identical influence on the whole of the solar cell surface.

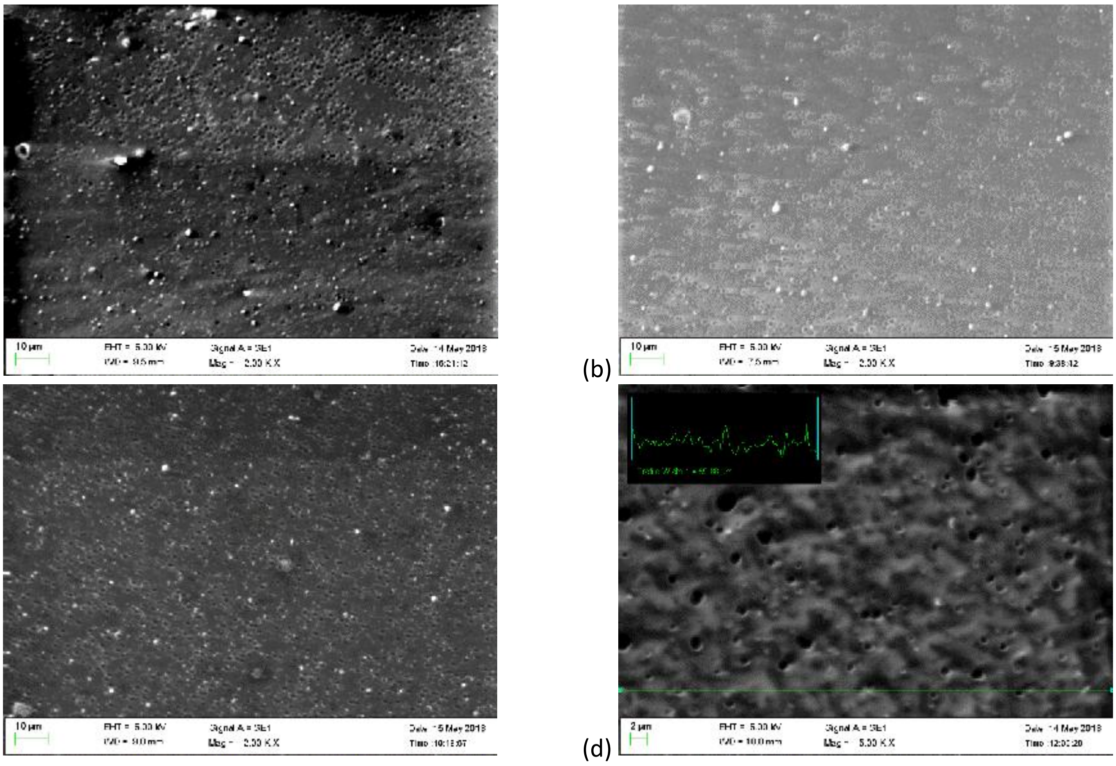
(a) (b) (c) (d)


Fig. 12. The secondary electron (SE) SEM image of down-conversion layer with ZnO NPs in concentrations of (a) 1%, (b) 2%, and (c) 5%, deposited at 4000 rpm spin speed and (d) the exemplary surface profile of the DC layer with ZnO NPs in a 1% concentration deposited at 1000 rpm spin speed.
Source: Authors

The back-scattered electrons (BSE) SEM images for DC layers with ZnO NPs in various concentrations are presented in Fig. 13. Information about distribution of ZnO NPs in the PMMA base matrix in the DC layers is shown. The white points are ZnO NPs dispersed in the PMMA matrix (gray colour).

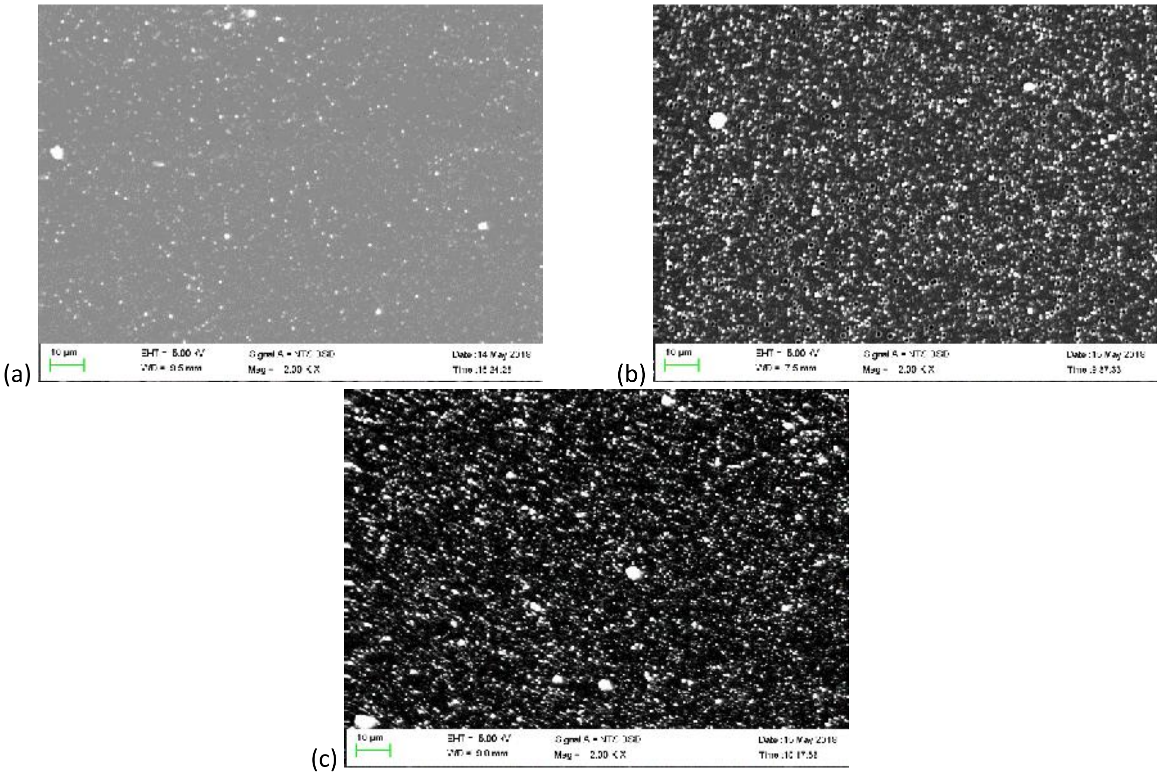


Fig. 13. Back-scattered electrons (BSE) SEM analysis of down-conversion layer with ZnO NPs in concentrations of: (a) 1%, (b) 2%, and (c) 5%, applied at 4000 rpm spin speed.
Source: Authors

Summary and conclusions

The photoluminescence effect could be successfully used in DC layers to increase solar cell efficiency. Based on Abrams et al. [10], Trupke et al. [11], and the results of computer simulation using SCAPS (Solar Cell Capacitance Simulator) software, the potential benefits of the DC layers are large. The photoluminescence properties and optical transmittance of DC layers are analysed as the two most important parameters. The luminescence quantum efficiency of the DC layer should be relatively high and the photoluminescence characteristic (excitation and emission spectrum) should match solar cell properties to increase the efficiency of the solar cell. In other words, the excitation spectrum should fall within the UV radiation and the emission spectrum should match EQE characteristic of a solar cell. The optical transmittance should be relatively high in the whole visible range.

The manufactured DC layers containing ZnO NPs dispersed in the PMMA matrix possess the desirable optical transmittance which exceeds 85% in the visible range for all layers, regardless of the concentration of ZnO NPs deposited at a spin speed of 4000 rpm or more. The emission spectrum of the DC layers achieves the highest values for higher concentrations of ZnO NPs when deposited at low spin speeds. As a compromise, a DC layer with a 5% concentration of ZnO NPs applied at 3000 rpm spin speed was chosen. As the next step, that DC layer will be applied on different photovoltaic structures and the basic parameters, including I-V and EQE characteristics of prototype solar cells with the DC layer will be examined.

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