Advanced nanostructured materials and their application for improvement of sun-light harvesting and efficiency of solar cells

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Abstract This review describes the application of different nanostructured materials in solar cells technology for improvement of sun-light harvesting and their efficiency. Several approaches have recently been proposed to increase the efficiency of solar cells above the theoretical limit which are based on a “photon management” concept that employs such phenomena as: (i) down-conversion, and (ii) surface plasmon resonance effect (iii) decreasing of the loss due to the reflection of the radiation, (iv) increasing of the reflection from the back contact, v) increasing of the effective solar cells surface, etc. The results demonstrate the possibility for to increasing of light harvesting, short circuit current and efficiency by application of nanomaterials in thin film and hetero-junction (HJ) solar cells. The first promising results allow an expectation for application of advanced nanomaterials in the 3rd generation solar cells.

1. Introduction

Improvement the efficiency and decreasing the production cost of terrestrial photovoltaic devices is important for their widespread application as a power generator. Because the immense potential of solar radiation it was predicted that photovoltaic will become a very serious alternative for electricity generation in the nearest future. Additionally, the problems such as energy independence and security, stability of energy supply and variety of energy sources which become much more vital these days can be overcome applying the electricity from photovoltaic conversion in the energy mix.

The unique properties of nano-sized materials with fitted low size can improve the light harvesting by the solar cells (SCs) and thus their efficiency. Different effects due to the nano-size of the materials can be applied for improvement of the parameters of SC. Several light trapping approaches (“photon management concepts”), which include random [1] and periodic textures [2], plasmonic nanoparticles [3,4], spectral modification of the incident light applying rear earth ions [5] have been studied. In addition, application of nanostructures, such as nanorods (NRs) [6,7] and nanowires [8] in thin film solar cells technology has attracted a lot of attention, in particular because of the possibility for increasing the light harvesting and, as well as, for decreasing of the carrier collection path [9].

This review-paper presents the results of the study of the optical and structural properties of dielectric thin film SiO2 with embedded Tb*, applied as a down-convertor to thin film solar cells, multilayer structure ZnO:Al/Ag/ZnO:Al as a back reflector with plasmonic scattering effect and, as well as, electrochemically deposited ZnO with NRs array as antireflection coatings and substrates with increased diffused reflection. The comparison of the parameters of the solar cells without and with applied nanomaterials demonstrates improvement of the external quantum efficiency, increasing the short circuit current and efficiency and of Si thin film solar cells.
2. Experimental, results and discussion

2.1. Down conversion

Almost of the attempt to improve of the solar cell efficiency to date have aimed at modifying the structure of the solar cells itself by fitting its spectroscopic sensitivity to the fixed sunlight spectrum. A reverse concept, however, is to fit the sunlight spectrum to the solar cell sensitivity via a wavelength-shifting operation. This can be done, e.g. by the inclusion of layers containing rare earth ions on the front of the SC. Because the glass, the front contact layer and the doped layer absorb in the blue and near UV spectral range the solar cells and PV modules with glass as a cover or SCs in superstrate configuration have a poor response in this wave-length range. The efficiency of thin film solar cells can be improved with the addition of a photon down-conversion top layer which have absorption bands in the UV region and emission bands in the visible region (in the best case at the spectral sensitivity peak of the Si solar cells).

An example with application of SiO$_2$:Tb thin films as a down convertors is presented here. The sketch of a- Si:H/c-Si (so called hetero-junction) solar cell with a down-convertor on its top is shown in figure 1.

![Figure 1. The sketch of a-Si:H/c-Si solar cell with a down-convertor.](image)

SiO$_2$:Tb thin films with Tb concentration of 1% [5] are deposited by magnetron co-sputtering on suprasil substrates and are annealed at different temperature 600°C, 700°C, 750°C and 850°C in atmosphere of N$_2$. The TEM picture of SiO$_2$:Tb thin films annealed at 600°C is presented in figure 2, the size of Tb nanoclusters is in the range of 20-70 nm. The spectra of absorption (of the samples deposited on suprasil substrates) are measured before and after annealing (figure 3). The main absorption peak in the as-deposited films is at 224 nm and shifts slightly to 225 nm in the annealed samples. No significant difference is observed in the absorption spectra for the samples annealed at different temperatures. The FWHM of the main absorption peak at about 223-224 nm slightly decreases after annealing and the broad absorption bands at about 323 nm and 760 nm disappeared. The spectra of photoluminescence (PL) excited with $\lambda = 337$ nm are presented in figure 3. Peak of PL at about 550 nm is observed and its intensity is maximal for the sample annealed at 600°C (figure 3). This emission band is due to the $^5D_4$ to $^7F_5$ transition in the Tb$^+$ [5 and the references there].

![Figure 2. TEM picture of magnetron co-sputtered SiO$_2$:Tb thin films annealed at 600°C.](image)

![Figure 3. Spectra of absorption (a) and PL (b) of SiO:Tb films.](image)
SiO$_2$:Tb films deposited on suprasil substrates are positioned on top of an a-Si/c-Si-hetero-junction solar cell structure (figure 1). The spectra of external quantum efficiency (EQE) and EQE ratio of the solar cells measured with and without SiO$_2$:Tb film on the top of the cells demonstrate slight increasing of the EQE in the UV range due to the PL of the Tb$^+$ more pronounced for the cell D411-Q-1-BS/suprasil (figure 4).

2.2. Multilayer stacks ZnO:Al/Ag/ZnO:Al as back reflector with plasmonic scattering

It has been reported that the back reflector with plasmonic Ag nanoparticles situated between two metal oxide layers, like ZnO, TiO$_2$ (multilayer stacks) can provide light-trapping performance comparable to the reported for n-i-p a-Si:H solar cells with applied random texture [10]. An advantage of the multilayer structure is that using the metal oxide in the plasmonic stacks with Ag nanoparticles prevents the parasitic effect as charge recombination on metal in the case when the nanoparticles are deposited directly on Si layer [11].

Figure 5. TEM micrographs of as-deposited (a and c) and annealed (b and d) multilayer stacks ZnO:Al(20nm)/Ag(x)/ZnO:Al(20nm) with different thickness of the Ag film for x= 16 nm (a and b) and 20 nm (c and d). The markers correspond to 200 nm [12].

It is demonstrated that the stack structure deposited by magnetron sputtering of thin films ZnO:Al (from ZnO:Al target) and Ag layer (from Ag target) between them with thickness of Ag layer x > 12 nm have a very low resistivity (< 5 $10^3$ Ω cm) [12]. The TEM pictures (figure 5) show that the Ag nano-particles

Figure 6. Spectra of reflectance of multilayer stack structures ZnO:Al(20nm)/Ag(x)/ZnO:Al(20nm): as-deposited (a and b) and annealed (c and d), for x=6 nm (curves 1), 10 nm (curves 2), 12 nm curves (3), 16 nm (curves 4) and 20 nm (curves 5) [12].
(NPs) form aggregates into chains in the stacks with \( x = 16 \) nm and the structure of Ag film transforms from discontinuous into semi-continuous for \( x = 20 \) nm. The annealing of the structure results in increasing of the Ag grain size due to the coalescence. The transmittance and reflectance spectra of the as-deposited and annealed films presented in figure 6 demonstrate bands at about 365 nm due to Ag electrons plasma oscillations and near lying inter-band d-shell electron transitions of the electrons [11]. The position and the width of the bands depend on the Ag NPs size and shape distribution in the middle Ag films which are determined by the thickness of the Ag film and the process of annealing. The same bands associated with the plasmonic effect and d-shell electrons inter-band transitions are observed in the spectra of haze ratio in transmission and reflection. The as-deposited stacks with thickness of the middle Ag films of 16 and 20 nm demonstrate high conductivity, high value of reflectance and plasmonic light scattering [4,12]. The application of the ZnO:Al(20nm)/Ag(20nm)/ZnO:Al(20nm) as back scattering reflector results in increasing of short circuit current of Si solar cells on the basis of poly-Si films (figure 7 and table 1). It is seen that the short circuit current, \( J_{sc} \), relative increasing is 10\% and 133\% in the case of as-deposited stack with Ag thickness of 16 and 20 nm, respectively and 54\% - in the case of annealed stack with \( x = 16 \) nm. All presented data are average taken from measurement of 6 solar cells. The increasing of the \( J_{sc} \) is due to the increased reflection of the stacks with plasmonic properties applied as back reflector in Si thin film solar cells which is related to the optimal size, shape and distribution of the Ag nanograins [13].

**Table 1.** Relative average increases of the \( J_{sc} \) in thin film Si solar cells with plasmonic stack.

| Samples | Plasmonic structure | Thicknesses, (nm) | Annealing | Relative \( J_{sc} \) average increases |
|---------|---------------------|-------------------|-----------|--------------------------------------|
| TFP8    | ZnO:Al/Ag NPs/ZnO:Al| 20/20/20          | as deposited | ~ 133\%                              |
| TFP1    | ZnO:Al/Ag NPs/ZnO:Al| 20/20/20          | annealed   | ~ 0\%                                |
| TFP5    | ZnO:Al/Ag NPs/ZnO:Al| 20/16/20          | as deposited | ~ 10\%                               |
| TFP4    | ZnO:Al/Ag NPs/ZnO:Al| 20/16/20          | annealed   | ~ 54\%                               |

2.3. ZnO nanorods as antireflection coating in Si heterojunction solar cell

The ZnO based nano-structured (NS) layers with nanometer sized features have highly developed surface areas per unit volume. In order to fabricate solar cells with increased efficiency the ZnO films have to have such a future size on the surface that will define high light harvesting, light scattering and optical confinement [12]. It has been reported that ZnO nanorods array demonstrates antireflecting properties leading to decrease of the specular and diffused reflection of the substrate they are deposited [14,15]. One of the attractive methods for fabrication of ZnO nanostructured array is electrochemical deposition because it is a simple and low cost method and is suitable for industrial large-scale application.

ZnO nanostructured (NS) array layers are deposited as ARC on the front side of silicon heterojunction...
Figure 8. The scheme of the SHJ solar cells with ZnO NSs (left) and SEM of the ZnO NS array deposited on the samples 1-C6 (a and d), 1-C4 (b and e) and 1-C2 (c and f) given in two different magnifications. The markers correspond to 8 µm (a, b and c) and 800 nm (d, e and f) [15].

(SHJ) solar cells with ITO as a front side transparent electrode: Ag grid/ITO/(p)a-Si:H/(i)a-Si:H/(n)c-Si/(i)a-Si:H/(n+)a-Si:H/Al [16]. ZnO nanostructured array films are grown by an electrochemical process from aqueous solution of ZnCl$_2$ (5. $10^{-4}$ M) and KCl (1 M) with pH $\approx$ 6.0 at 80$^0$C using a three-electrode electrochemical cell as described in [17]. The solar cell was used as one of the electrode – the cathode. Spectrally pure graphite electrode was used as anode. The electrolyte was agitated by magnetic stirrer. The SEM micrographs of the ZnO nanostructures grown on 3 different solar cells (figure 8) demonstrate difference in the surface morphology of the grown ZnO NS array is mainly due to the different conditions

Figure 9. Spectra of specular reflectance (a, b, c) and diffused reflection (d, e, f) of samples 1-C6 (a, d), 1-C4 (b, e) and 1-C2 (c, f) without and with deposited ZnO NS array film [15].
Table 2. The deposition conditions of the ZnO NS array films and comparison of the parameter of the SHJ before after ZnO NS growth.

| Solar cells parameters | 1-C2   | 1-C4   | 1-C6   |
|------------------------|--------|--------|--------|
| $I_{sc}$ (mA), with ZnO NS | 30.637 | 30.689 | 30.237 |
| $I_{sc}$ (mA), without ZnO NS | 30.514 | 29.839 | 28.979 |
| $\Delta I_{sc}$ (mA), relative increasing | 0.123  | 0.850  | 1.258  |
| $V_{oc}$ (mV), with ZnO NS | 695    | 694    | 689    |
| $V_{oc}$ (mV), without ZnO NS | 697    | 697    | 691    |
| FF, (%) , with ZnO NS | 72.74  | 72.90  | 71.61  |
| FF, (%) , without ZnO NS | 74.00  | 73.50  | 73.02  |
| $\Delta V_{oc}$, (%) | 1.26   | 0.60   | 1.41   |
| $\eta$, (%) , with ZnO NS | 15.492 | 15.535 | 14.917 |
| $\eta$, (%) , without ZnO NS | 15.733 | 15.278 | 14.521 |
| $\Delta \eta$, (%) | -0.241 | 0.257  | 0.396  |
| $\Delta \eta$, relative changes | -1.5   | 1.68   | 2.7    |
| $t$, (min) | 1.5    | 1.5    | 1.5    |
| $I_{el.-chem}$, (mA) | 3      | 6      | 6      |
| $U_{el.-chem}$, (mV) | 1000   | 1000   | 950    |

applied during electrochemical deposition on solar cells and to the slight difference in the thickness and resistivity of the surface ITO layer. In the case of samples 1-C6 and 1-C4 the nanorods sized about 100-200 nm are distributed in different surface area with different density. The SEM of the sample 1-C2 reviles the presence of largest nano-ZnO features about 800 nm with relatively large distance between them.

The spectra of specular reflectance and diffused reflection of the three samples of the series, before and after the deposition of ZnO nanostructured array films, presented in figure 9 show that the values of reflectance decrease which is more pronounced in the sample 1-C6. The value of diffused reflection decrease in the samples 1-C6 and 1-C4 and increase in the case of sample 1-C2. The differences in the surface morphology and microstructure of the textured ZnO films determine the difference in the optical reflection properties [18].

The study demonstrates that the ZnO nanostructured array films grown on the front side of the SHJ solar cells act as ARC leading to decreasing of the reflectance, improvement of the short circuit current (by about 4.3 %) and efficiency (by about 2.7%) of the thin film SHJ solar cells (table 2). An improvement in the short circuit current and efficiency of the SHJ solar cells is achieved in the samples where the values of reflectance and diffuse reflection decrease after ZnO NS array films deposition on the front side. The higher increase in $J_{sc}$ and efficiency, $\eta$, is higher in the samples where larger decreasing of the values of reflectance and diffuse reflection are obtained as a result of deposition of ZnO NS array films leading to improvement of the ligh harvesting [14,15].

2.4. ZnO nanorod array as a substrate in thin film solar cells

The ZnO nanorods (NRs) prepared by an electrochemical process are implemented in the n+i-p⁺ a-Si:H solar cell on flexible stainless steel (SS) foil, aiming at increasing the $J_{sc}$ without deterioration the open

Figure 10. AFM (a) and SEM (b) pictures of ZnO NRs array on SS substrate.
circuit voltage, $V_{oc}$, and the fill factor, $FF$ [7]. Figures 10 a and b show the AFM and SEM images. The surface morphology consists of nanorods with diameter size of single NR between 200 and 500 nm [7] and high of about 200-300 nm. The thin film solar cell structure deposited on such kind of flexible substrate is

**Figure 11.** Spectra of diffused reflection, total reflection and haze in reflection of ZnO NRs array deposited on different structured SS substrates [7].
Table 3. Parameters of thin film a-Si:H solar cells with different scattering substrates [7].

| N | Substrate structure | $V_{oc}$, mV | $J_{sc}$, mA/cm$^2$ | FF | Eff. |
|---|---------------------|--------------|--------------------|-----|-----|
| 1 | SS/BR               | 857          | 11.4               | 0.61| 6.02% |
| 2 | SS/BR/NR            | 803          | 13.4               | 0.47| 5.11% |
| 3 | SS/BR/NR/BR         | 850          | 13.8               | 0.62| 7.28% |
| 4 | SS/Replica of Asahi-U texture/BR | 851 | 12.4 | 0.62 | 6.56% |

SS/back reflector (BR)/n-type a-Si:H/i-a-Si:H/p-μc-Si:H/ITO/Ag grid. The BR consists of a stack of Ag and AZO, with thicknesses of respectively 300 nm and 80 nm. In addition to the components of the basic BR (figure 11 a), there is the scattering medium consisting of either ZnO NRs (figure 11 b) and ZnO NRs coated by a stack of Ag (300 nm) and AZO (80 nm) (figure 11 c) or a nano-imprinted replica of Asahi-U texture (figure 11 d).

The spectra of reflectance, diffused reflectance and haze in reflectance of four back reflectors on SS substrate are shown in figure 11. The highest value of haze ratio in reflectance demonstrates the BR with ZnO NRs covered by two layers structure Ag (300 nm thick) and ZnO:Al (80 nm thick). The parameters of the solar cells obtained from I-V characteristics demonstrate that when the solar cell is deposited on ZnO NRs (figure 11 b) the $J_{sc}$ is increased by 2 mA/cm$^2$ (table 3). Since the ZnO NRs are not doped and thereby very resistive, the solar cell of No. 2 with a-Si:H grown directly on ZnO NRs has low FF and $V_{oc}$. When the ZnO NRs are coated with Ag and AZO, the solar cell shows 2.4 mA/cm$^2$ higher $J_{sc}$ than the reference cell of No.1, and 1.4 mA/cm$^2$ higher $J_{sc}$ than the cell of No. 4 deposited on substrate with the nano-imprinted replica of Asahi-U texture, and highest value of efficiency and no deterioration of the $V_{oc}$ and FF. The optical enhancement of the solar cell by ZnO NRs is explicitly demonstrated in the EQE spectra in figure 12. The ZnO NRs enhance the EQE response in the wavelength range from 400 nm to 800 nm.

Figure 12. EQE spectra of thin film Si:H solar cells on different scattering substrate [7].

Conclusion
The results in this review article show that proposed novel solar cell architectures that make use of nanomaterials have demonstrated increasing light harvesting and improvement of the parameters of the solar cells as a result of the effects due to the nano-scaled structures. The third generation of solar cells with application of nanomaterials as low cost and high efficiency revolutionary technologies needs to be developed to make photovoltaic energy economically competitive. Future advances and the rate at which we can achieve large scale application of the new effects will depend entirely on the amount of resources the society chooses to invest in nanotechnology and photovoltaics.

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