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Optical and structural properties of electrochemically deposited ZnO nanorod arrays suitable for improvement of the light harvesting in thin film solar cells

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Optical and structural properties of electrochemically deposited ZnO nanorod arrays suitable for improvement of the light harvesting in thin film solar cells

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Abstract. The results of study of the optical and structural properties of ZnO nanorods (NR) arrays electrochemically deposited on two type substrates - the ITO surface on the front side of Si heterojunction (SHJ) solar cells and on stainless steel plate used for formation of a-Si:H thin film solar cells, are reported. The surface morphology of the NS arrays is examined by Scanning Electron Microscopy and AFM. The spectra of specular diffused and total reflection, and haze ratio in reflectance are compared before and after deposition of the ZnO NR arrays. In the case of deposition on ITO surface of SHJ solar cells the values of the direct and diffused reflection of the ZnO NR array decrease demonstrating good antireflection properties. Deposition of ZnO NS arrays on stainless steel plates leads to increasing the values of the diffused reflection and the total reflectance. Possible application of ZnO NS structures for the processing of advanced Si based solar cells for increasing light harvesting is discussed.

1. Introduction

Increasing the efficiency and decreasing the production cost of terrestrial photovoltaic devices is important for the further development and widespread of the photovoltaic technologies. Solar cells made applying nanostructured and new emerging materials are being investigated to address this challenge. One of the ways to get higher efficiency of solar cells is to increase the optical absorption by light trapping. This could be achieved by implementation of nanomaterials: i) for decreasing the reflection of the light from the front side of the solar cells [1-2] and, as well as, ii) for increasing the reflection and scattering of the passed through the solar cells light by three dimensional (3D) back side surface [3]. Additionally, the nanometer size objects have very large surface areas per unit volume which offers the possibility to form very large interfacial area resulting in increasing the charge carrier collection, the generated current and the efficiency of the solar cells due to the 3D geometry of vertical aligned nanostructured features as nanorods and nanowiskers [4, 5].

ZnO is material widely used for thin film solar cells. It can be grown in the large nanostructured arrays by a low cost method as electrochemical deposition [6, 7].

This work reports the results of study of the optical and structural properties of ZnO nanostructures on two type of substrates – on the ITO on the front side of the Si heterojunction (SHJ) solar cells - Ag grid/ITO/a-Si/c-Si/Al [8] and on the stainless steel plates to be applied as substrates for

thin film a-Si:H solar cell deposition [9]. The obtained changes in the optical spectra of specular and total reflectance, and diffused reflection are discussed regarding the possible applications of the nanostructured ZnO arrays.

2. Experimental

ZnO nanostructured films were deposited on the front side of the heterojunction solar cells by an electrochemical process from aqueous solution of $ZnCl_2$ (5. 10^{-4} M) and KCl (1 M) with pH≈5.0 at 90^0C for for1 min - in the case of growing on the ITO face of SHJ; and at 60^0C for 30min – in the case of deposition on stainless steel plate using a three-electrode electrochemical cell with SCE as a reference electrode. As a working electrode SHJ solar cells and stainless steel plates were used. Spectrally pure graphite rod electrode was applied as anode. The electrolyte was agitated by magnetic stirrer.

Deposited zinc oxide layer could be suggested to be a product of interaction of OH^- and Zn^{2+} in aqueous solution on the surface of the electrode (equation 1). Since the zinc hydroxide is unstable, it does dehydrate into ZnO [10]:

$$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2 \rightarrow ZnO + H_2O \quad (1)$$

The process was carried out controlling the redox potential of the high power potentiostat system WENKING HP 96. The deposition potential was kept at -1000 mV (vs. SCE). The oxygen content in solution was permanently measured and the redox potential was kept in the range 300-400 mV (vs. SCE), oxygen is provided in the system by supplement of H_2O_2.

The optical spectra (specular reflection, diffuse reflection) of the deposited arrays were measured by a spectrophotometer Shimadzu UV-3600 in the range of 300 - 1200 nm employing a 60 mm integrated sphere. The surface morphology studies were performed by a Scanning Electron Microscope (SEM) Philips 515 and by AFM apparatus NT-MDT Solver 47 Pro system in a “semi-contact” (taping) mode.

3. Results and discussion

3.1 ZnO nanostructures (NS) deposited on ITO front contact of SHJ solar cells

The ZnO nanorod arrays are electrochemically deposited on the front side (ITO layer) of the heterojunction solar cells - Ag grid/ITO/a-Si/c-Si/Al. In this case the deposition time is 1 min. As we reported earlier the XRD diffraction study of the deposited ZnO by this technique reveals the existence of ZnO with hexagonal wurtzite structure [11]. The SEM micrographs with different magnifications of the deposited ZnO nanostructured arrays are demonstrated in figure 1.

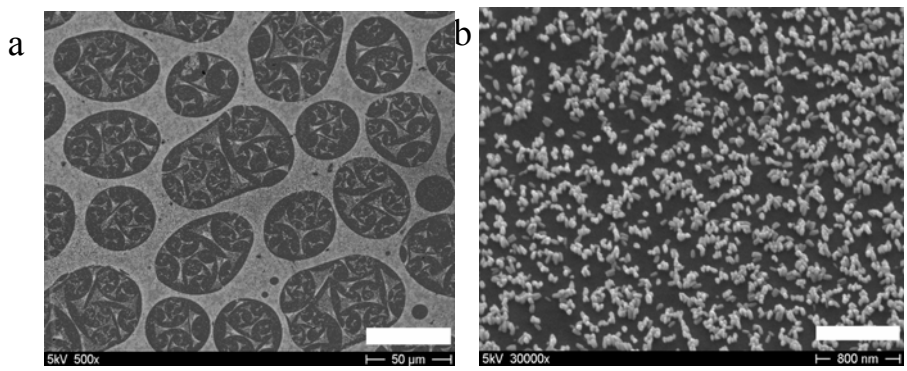

Figure 1. SEM of ZnO NS deposited on ITO front side of SHJ solar cell with different magnification. The markers correspond to 50 µm (a) and 800 nm (b).

The grown ZnO consists of nanograins which are distributed very inhomogeneous on the surface of the substrate – in the less dense large spot-like areas sized of several tens of μm^2 with rarely located grains are seen (figure 1a). It is seen clearly that on the surface of the denser areas the grains have size of about 60-80 nm and the distance between them is in the range 50 - 400 nm (figure 1b).

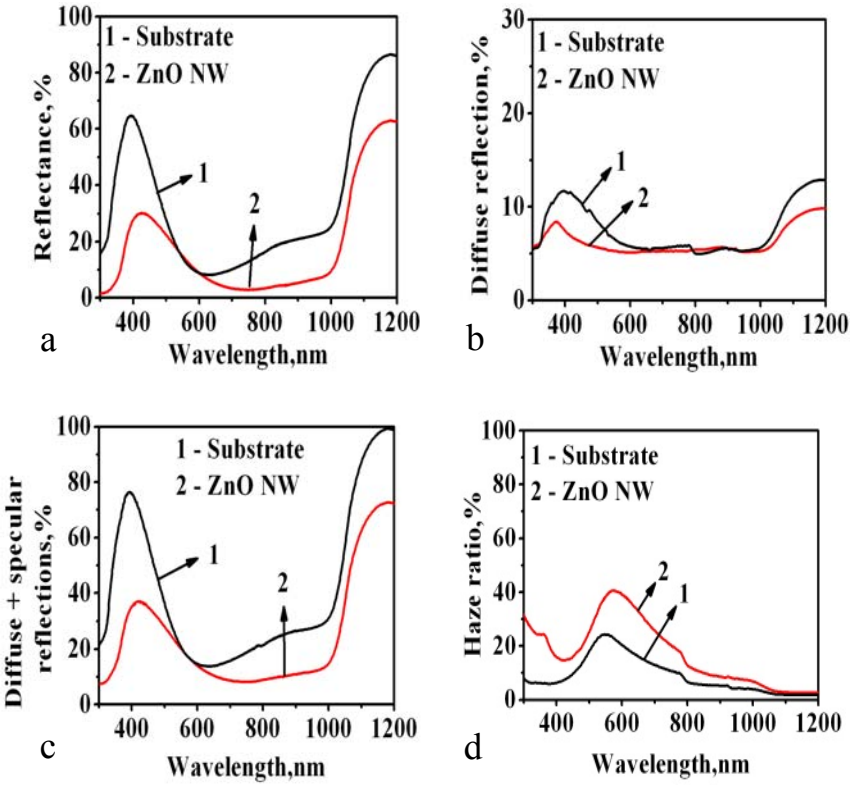

Figure 2 Spectra of reflectance (a), diffused reflection (b), total reflection ($R + R_{dif}$) (c) and haze ratio in reflectance (d) of ZnO NS array layer deposited on front side of SHJ solar cell. The corresponding spectra of the substrate before ZnO NS deposition are shown, as well, for comparison.

Figure 2 shows the spectra of specular reflectance (R_{spec}), diffused reflection (R_{dif}), total reflection ($R_{tot} = R_{dif} + R_{spec}$) and haze in reflectance (H_R) of the ZnO NR arrays grown on the front side of the SHJ solar cell. The haze ratio in reflectance is defined as a ratio of the diffused to total reflection:

$$H_R = R_{dif}/(R_{dif} + R_{spec}) \quad (2)$$

The values of reflectance and total reflection decrease after deposition of ZnO NR arrays. In the spectra of diffused reflection decreasing is observed in the wave length ranges: 350-650 nm and 1000-1200 nm.

Decreasing the values of the specular (figure 2 a) and total reflection (figure 2 c) and increasing the haze ratio in reflection (figure 2d) are seen in almost the whole spectral region. It should be noted that the maximal drop of reflection in the whole spectral region under investigation is observed for the sample with grain size of ZnO NRs of 60-80 nm (figure 1 b) deposited for 1 min on the front side of the SHJ solar cell compare to the other samples where the deposition time is longer as reported earlier [12]. The ZnO NRs arrays studied in this work demonstrate good antireflection (AR) properties. The minimal values of reflectance of about 2.5- 3% are observed in the larger spectral range 650-850 nm

(figure 2a) than to the results showing minimum value of reflectance – 3-4 % only at 667 nm as reported by other authors for the ZnO NRs arrays with 50-60 nm diameter size of the NR obtained by solution grown on poly-Si substrates [13]. The study of the I-V characteristics of SHJ solar cells before and after deposition of ZnO NR arrays for 1 min shows improvement in the values of the short circuit current by 3.371 mA/cm^2 and of the efficiency by 1.6%, which correspond to relative increasing of 12.6% and 14.2%, respectively, after deposition of ZnO NR arrays. This is due to the decreasing of reflection from the front side of the solar cell and increased light harvesting earlier reported by us [12], which values are higher than those shown in [13, 14].

3.2 ZnO nanostructures (NS) deposited on stainless steel plates

Figure 3 demonstrates the SEM micrograph and AFM picture of ZnO nanorod arrays deposited on stainless steel plate. The hexagonal ZnO nanorods with size about 100-500 nm are grown almost perpendicularly to the substrate.

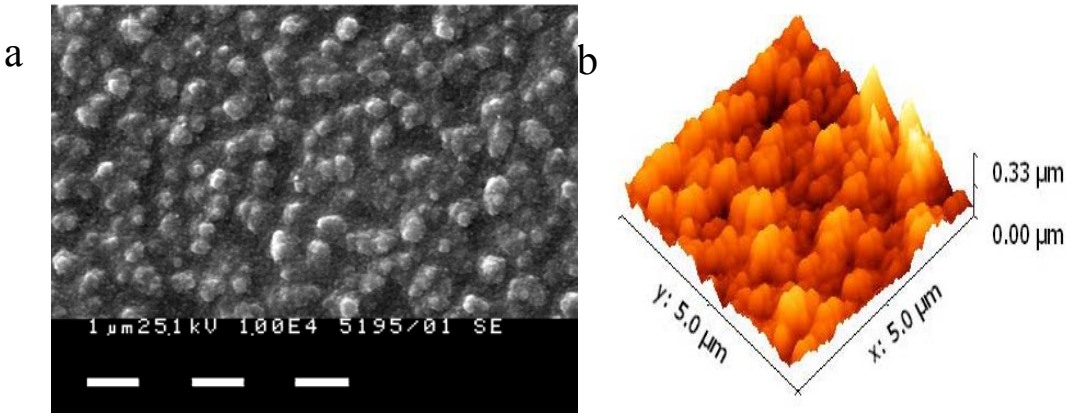

Figure 3. SEM micrograph (a) and AFM picture (b) of the ZnO layer electrochemically deposited on stainless steel plate.

They are relatively homogeneously grown on the whole surface area of the substrate. The ZnO NRs have different height with maximal size of about 300 nm (figure 3b). The estimated mean roots square roughness obtained from AFM measurement is 120 nm.

The spectra of specular reflectance, diffused reflection, total reflectance and haze ratio in reflectance of the ZnO NR arrays grown on stainless steel plate are shown in figure 4. It is seen that after deposition of ZnO nanorods array the values of reflectance increase for the wave length > 600 nm and diffused reflection and total reflectance values increase in the visible range 500-800 nm.

The haze ratio in reflectance of the ZnO nanorod array is higher compared to the values of the substrate in the spectral range 400 - 650 nm where the values of the specular reflection are lower than those of the substrate. The higher values of the diffused reflection and of the total reflectance after ZnO NRs growth on the stainless steel substrate could be explained by the optimal for maximal absorption of the light diameter size of the ZnO nanorods and surface roughness.

As is reported in [2] the 3D approach for modeling of the performance of the pin a-Si:H solar cells with AR ZnO NR arrays shows that the values of the nanorods diameter size of 150 nm and the surface roughness of 120 nm are optimal for the maximal absorption of the light by the rough surface. The size of the diameter of ZnO NRs grown on stainless steel plate, object of investigation in our work, is 100-500 nm and the surface roughness is 120 nm, which values are close to the optimal theoretical ones calculated in reference [2].

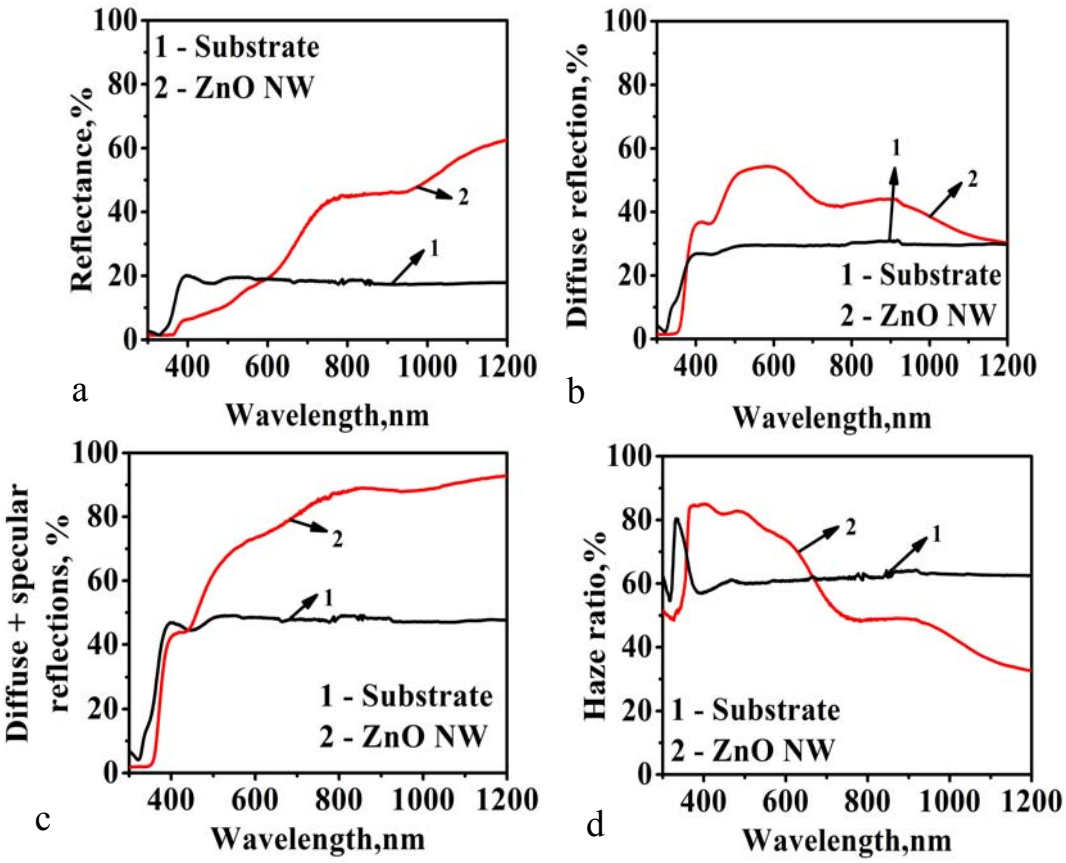

Figure 4. Spectra of reflectance (a), diffused reflection (b) and haze in reflection (c) of ZnO NS layers electrochemically deposited on stainless steel substrates. For comparison the corresponding spectra of the seeding stack structures (curves 1) are presented, as well.

Stainless steel plates with ZnO nanorod arrays are used as substrates for n-i-p a-Si thin film solar cells with ITO and Ag grid as front electrode, and Ag/ZnO:Al back reflector deposited on the substrate stainless steel/ZnO NRs arrays [9]. The preliminary results demonstrate that the J_{sc} of the solar cell with ZnO NRs is 2.4 mA/cm^2 higher than that of the solar cell without ZnO nanorods. It has to be notice that the comparison to the cell with nano-imprinted replica of Asahi-U texture, the J_{sc} gain is 1.4 mA/cm^2 [9]. These improvements correspond to relative increasing in the short circuit current and the efficiency by about 20% compare to the solar cells grown on the SS substrate without ZnO nanorods and about 10% compare to the reference cell deposited on SS substrate with nano-imprinted replica of Asahi-U texture at the rear side [9]. The improvement of the solar cells parameters can be explained by the increased diffused reflection and total reflectance of the substrate with ZnO NRs leading to higher light harvesting due to the suitable three-dimensional geometry of the nanorod arrays. Additionally, the larger effective area of the thin film solar cell deposited on the substrate with ZnO NRs arrays results in increasing the light trapping as well.

Conclusion

In this work the surface morphology and the optical properties of electrochemically deposited ZnO nanorod arrays on ITO on the front side of the SHJ solar cells and on the stainless steel plates applied as substrate for deposition a-Si:H thin film solar cells. The ZnO nanostructures arrays consist of nanorods with diameter size of 60-80 nm in the case of growing on the ITO front side of the SHJ solar cells and of about 100-200 nm when they are grown on stainless steel plate. Decreasing of the reflectance, diffused and total reflection after deposition of the ZnO nanorods on the front side of the

SHJ solar cells is observed. Due to the good anti-reflection properties of the deposited ZnO nanorod arrays the short circuit current and the efficiency of the SHJ solar cells are improved by 3.37 mA/cm^2 and of the efficiency by 1.6%, which correspond to relative increasing of 12.5% and 14.2 %, respectively. The ZnO nanorod arrays deposited on stainless steel substrates result in increasing of the diffused reflection and haze ratio in reflectance in the visible range of the spectra due to the appropriated size of the ZnO NRs and the roughness of the deposited nanostructured arrays used as substrate for deposition of a-Si:H solar cells. The relative improved by about 20% photocurrent and efficiency of thin film a-Si:H solar cells deposited on the stainless steel substrate with ZnO NRs compare to the reference cells are explained by increasing of light harvesting due to the appropriate size of the nanorods in three-dimensional arrays.

Acknowledgements
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