Influence of the substrate material on the surface morphology of electrochemically deposited ZnO layers

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In this paper we report results of fabrication of ordered ZnO nanorods (NRs) or nanowalls (NWs) electrochemically deposited on different highly conductive substrates. The following types of conductive substrates have been used: (i) highly doped p-type multi-crystalline Si, and (ii) Copper thin plates. The influence of a seeding Ag layer deposited on multi-Si substrates on the growth of ZnO NRs has been studied as well. It is observed that morphology of the deposited ZnO structures depends strongly on the type of the substrate used. It is found that ZnO structures with different shapes, such as nanorods, nanotubes or nanowalls can be grown on top of highly conductive substrates used in this work. It is observed that optical reflection of the deposited layers depends on the substrate used as well as on the time of the electrochemical deposition of ZnO layers. It was found that: (i) for ZnO NWs/Cu structures, diffused reflection exhibit strong enhancement compared to pure Cu substrate; (ii) in case of ZnO NRs/Si structures reflection is decreased compared to that for pure Si substrate. Possible applications of ZnO NRs or NWs based structures for the processing of advanced Si based solar cells are discussed.

1 Introduction ZnO thin films and coatings have attracted a great interest due to their suitable properties for application in optoelectronic devices, sensors, displays and different thin film solar cells [1-4.] Recently, development of cost-effective methods for fabrication of one dimensional ZnO nanostructures, such as nanowires, nanorods and nanotubes have attracted extensive attention because of their potential applications for the advanced solar cell structures [5,6]. The nanometer size ZnO based nanostructures have very large surface areas per unit volume, which offers a possibility to improve light harvesting properties of solar cell structures in case if such nanostructures are used as antireflection coatings [5, 6]. ZnO based layers and nanostructures with different morphologies can be deposited by different techniques such as chemical and electrochemical deposition, sol-gel processing, spray pyrolysis, Vapor Liquid Solid (VLS), arc discharge, pulsed laser deposition etc. [5-13]. Electrochemical deposition is an attractive method for fabrication of ZnO nanowires because of its simplicity. Additionally it is a low cost method, which can be used on industrial scale.

This paper reports results of fabrication of one dimentional nanostructures (nanorods/nanowalls), obtained by electrochemical deposition of ZnO based layers on different conductive substrates (Si, Cu). According to our knowledge, highly doped p+ Si substrate is used for a first time as a substrate for electrochemical deposition of ZnO nanostructured films. p+-Si can be considered as: (i) an emitter for the n-type Si based solar cells and (ii) as supporting highly doped low-cost substrates for thin film a-Si:H based solar cells processed in a substrate configura-

tion. Such solar cells can be deposited on top of nanostructured ZnO/Si structures, which exhibit enhanced light harvesting properties.

An analysis of the surface morphology of such layers is performed by means of Scanning Electron Microscope (SEM). Measurements of the diffused reflection spectra of ZnO based nanostructures deposited on Si and Cu substrates have been performed as well.

2. Experimental ZnO nanostructured films have been deposited by means of an electrochemical process from acid aqueous solutions of $ZnCl_2$ (5. 10^{-3} M) and KCl (0.1 M) with pH 4.0 at temperature of 80 °C using a three-electrode electrochemical cell and saturated calomel electrode (SCE) as reference electrode. Since the potential of Zn in the electrolyte is −1.05 V vs. SCE the deposition process of ZnO is carried out at −1.0 V vs. SCE preventing a metal Zn deposition. Good quality ZnO films have been obtained at a redox potential within the range between +0.30 and +0.40 V vs. SCE. Zinc peroxide (ZnO_2) was formed on the samples with bad adhesion to the substrate at a redox potential higher than +0.4 V. ZnO layer deposition time varies between 30 and 120 min. The thickness of the grown ZnO films estimated from cross section SEM images was in the range of 0.4 – 1.0 μm.

ZnO layers have been deposited on different types of conductive substrates, such as high conductive p-type multi-crystalline Si (multi-Si) substrates with resistivity ~ 100 mΩ/□. As-cut, as well as etched in Ar^+ r.f plasma Si substrates and Cu thin plates have been used. The influence of the presence of a seeding Ag layer deposited on the plasma etched multi-Si substrate has been studied as well. Multi-Si substrates with thickness about 200μm have been fabricated using wire sawing of a Si block obtained by casting method from a metallurgical grade Si feedstock. Si substrates have been heavily doped by Boron upon the Si ingot growth. Si substrates have been cleaned in acetone, isopropanol and deionized water followed by treatment in H_2SO_4+H_2O_2 solution and washing in deionized water before ZnO deposition. Another set of samples with electrodeposited ZnO layers has been prepared on Ag buffer film (8 or 15 nm) deposited by magnetron sputtering on polished multi-Si substrate. In case of 15 nm thick Ag layer an annealing at 230 °C for 50 min before the ZnO growth has been applied in order to form Ag nanodots, which have been used as nano-seeds upon the growth of the ZnO based nano-structures.

The surface morphology of the deposited ZnO based structures has been studied by means of Scanning Electron Microscope (SEM) Philips 515 and FEI Quanta 200F, and the thickness of the coating is estimated from the cross section images. Direct and diffuse reflection spectra have been measured by a spectrophotometer Shimadzu UV-3600 in the range of 300 – 2600 nm employing an integrating sphere for the diffuse reflection.

3 Results and discussion

3.1 ZnO on multi-Si Si substrates. Fig. 1 shows SEM surface images of the as-cut (Fig. 1 a) and plasma etched (Fig.1 b) multi-Si substrates. The as-cut multi-Si substrates have rough surface with large, relatively flat grains, which have size about 10–20 μm. Moreover, some smaller grains and particles, which have size about 2–3 μm can be also seen (Fig.1a). After Ar plasma etching Si surface of the multi-Si sample is rather smooth and consists of only large grains, which have size of about 10–15 μm. Fig. 2 shows SEM micrographs of ZnO layer

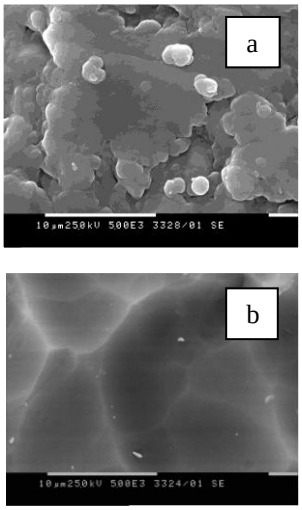

Figure 1 SEM images of the surface of as-cut (a) and plasma etched (b) multi-Si substrates**.** Markers correspond to 10 μm.

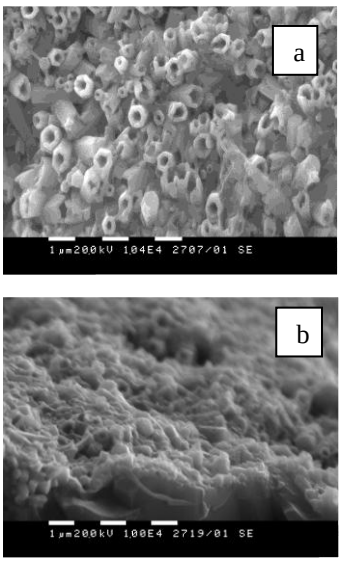

Figure 2 SEM images of the ZnO layer grown on as-cut multi-Si substrate at 80 °C and 1000 mV for 90 min: surface view (a) and cross section view (b). Markers correspond to 1 μm.

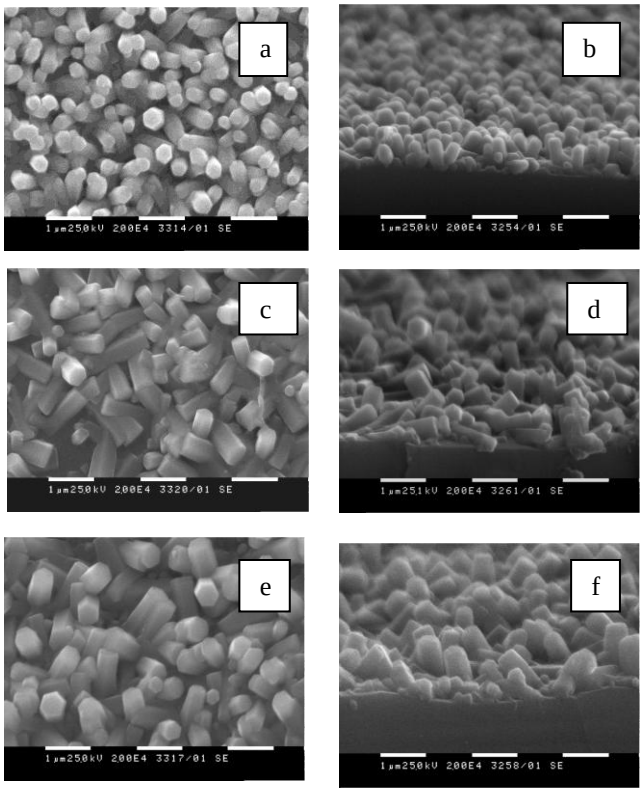

Figure 3. SEM images of the ZnO layer grown on plasma etched multi-Si substrate: surface view (a), (c) and (e) and cross section view (b), (d) and (f) deposited at 1000 mV and 80 °C for different time: 30 min – (a) and (b); 60 min – (c) and (d); 120 min – (e) and (f). Markers correspond to 1 μm.

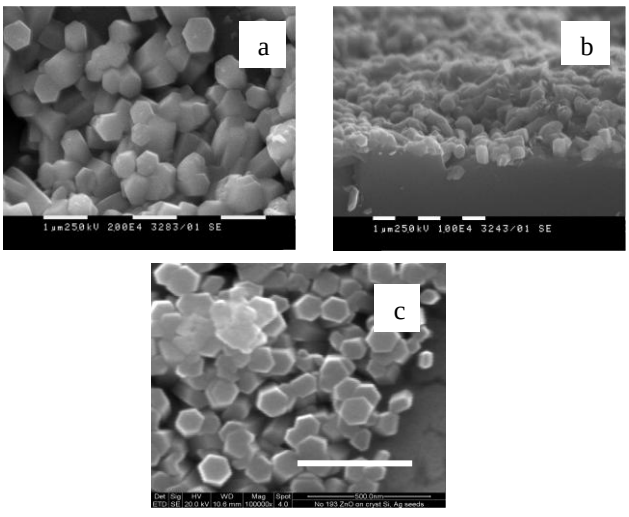

Figure 4. SEM images of ZnO grown on 8 nm seeding Ag layer deposited on polished multi-Si substrate at 80 °C, 1000 mV for 60 min: (a) – surface view and (b) – cross section; markers correspond to 1μm. For comparison the surface view of ZnO grown on 8 nm Ag layer deposited on c-Si substrate is given in (c) – marker corresponds to 500 nm.

grown on as-cut multi-Si surface. The grown layer consists of nano tubes, which have hexagonal shape and different diameters of about 200–600 nm (Fig. 2a). The averaged thickness of the layer is about 400 nm. The nanotubes have different orientation angles, which are caused by the high surface roughness of the multi-Si substrate. The surface morphology of the ZnO coating on a micron scale follows the morphology of the as-cut multi-Si substrate (Fig. 2b).

SEM images of ZnO layers grown on a plasma etched multi-Si substrate are shown in Fig. 3. From Fig. 3 it can be seen that the morphology of such layers is very different from that observed for ZnO layers grown on as-cut multi-Si substrates. Perfect hexagonal-like plane rods with an average diameter of about 400 nm and height of 500–1000 nm can be seen from Fig. 3 in this case. It has to be noted that an increase of the ZnO layer deposition time leads to the increase of the nano-rods height. Moreover, some bending of nano-rods with a larger height can be seen as well.

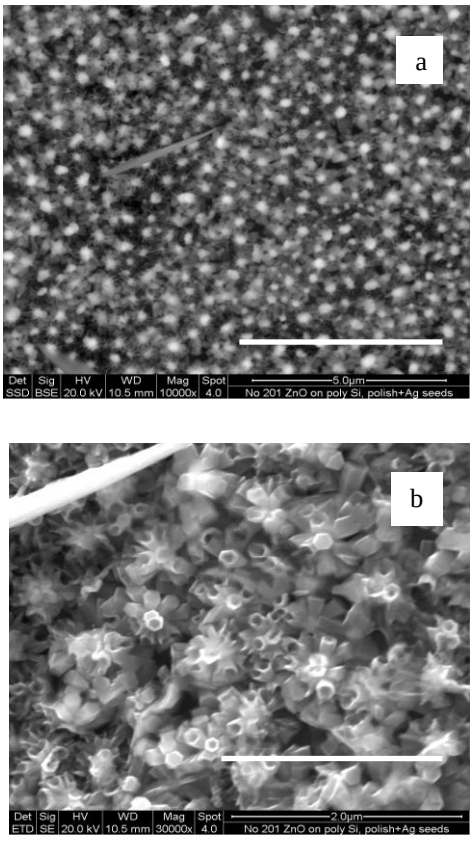

Figure 5. SEM images of the surface of ZnO nanorods and nanotubes (5b) grown on multi-Si substrate covered by buffer 15 nm Ag film annealed at 230^0C for 50 min (5a). Markers correspond to 2 μm (a).

3.2 ZnO on poly-Si substrate with Ag buffer layer Surface morphology of the ZnO nanorods grown on. 8 nm Ag buffer layer deposited by magnetron sputtering on plasma etched multi-Si substrate is demonstrated in Fig. 4 (a) and (b). From Figs. 4a, b it can be seen that hexagonal nanorods have very inhomogeneous distribution and different angles of growth on the surface of the Si substrate Diameters of ZnO NRs are about between 400 and 800 nm. Similar morphology has ZnO based structure, which is grown on 8 nm Ag buffer layer deposited on c-Si substrate, as it is shown in Fig. 4 c. However in this case the average size of the hexagonal NRs is about 200 nm, which can be explained by the different growth kinetics of ZnO NRs on a thin Ag layer compared to that for the case of Si substrates.

Deposition of ZnO film on top of 15 nm Ag buffer layers annealed at 230 ° C for 50 min results in a totally different morphology of the final ZnO based structure. In this case bunches of nanorods and nanotubes, 100–200 nm thick are formed as can be seen in Fig. 5 b. As shown in Fig. 5a, these structures start to grow from the Ag seeding nanodots, which have diameters of about 100–150 nm. These nanodots are formed after annealing of the Ag film.

3.3 ZnO on a Cu thin plate The surface morphology of ZnO structures grown electrochemically on Cu thin plates for different times is demonstrated in Fig. 6. From Fig. 6 it can be seen that ZnO structures deposited for 60 min consist of: (i) nanorods with diameters of about 150–200 nm; (ii) walls, which look like whiskers and situated between NRs. These walls have different lengths—from 1 to 2 μm and width (diameter) of about 200 nm. An increase of the deposition time up to 120 min leads to the disappearance of the ZnO nanorods and to formation of nano-walls (Fig. 6b,c).

From Fig. 6b and 6c it can be seen that the density and the height of the nanowalls are higher for the longer deposition times. It can be assumed that upon the longer ZnO deposition time the only growth of nanowalls occurs. It seems that the previously grown NRs (60 min growth) are transformed into nanowalls upon the longer electrodeposition process.

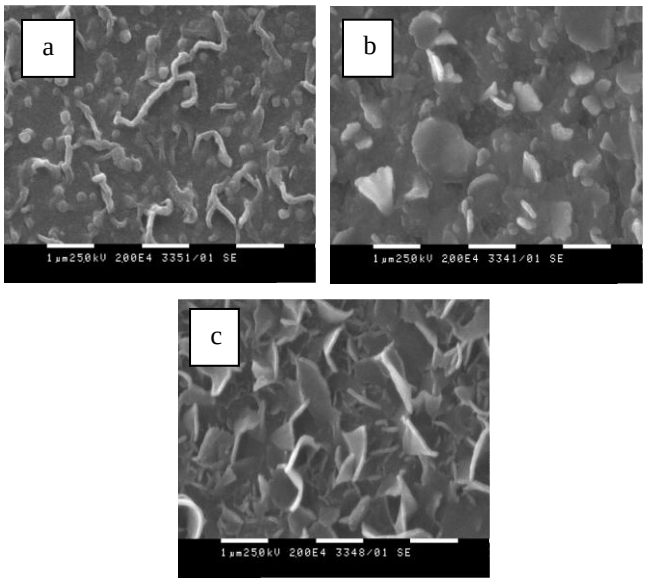

Figure 6. SEM images of the ZnO deposited by electrochemical grown on Cu thin plates for different time (a) – 60 min , (b) – 90 min, (c) – 120 min at 80 °C and 1000 mV. Markers correspond to 1 μm.

3.4. Diffuse reflection of ZnO grown on poly-Si susbstrate Diffuse reflection spectra of the deposited ZnO structures on multi-Si substrates are shown in Fig. 7. Reflection spectra have been recorded in the optical range of 350 – 1800 nm. For a comparison, reflection spectra of ZnO structures deposited on the as-cut (Fig.7, curve 1) and Ar^+ plasma etched multi-Si substrates (Fig.7, curve 2) are shown as well. It is seen that the plasma etching leads to an increase of the diffuse reflectance from the pure multi-Si substrate. However, ZnO layers grown on etched multi-Si exhibit lower values of the reflectance in the spectral region under investigation (Fig.7, curves 4, 5, 6 and 7). The only one exception has to be noted - in case of ZnO grown on plasma etched multi-Si substrate covered by 8 nm Ag seeding layer (Fig.7, curve 3), slightly higher reflectance values compared to those for pure plasma etched

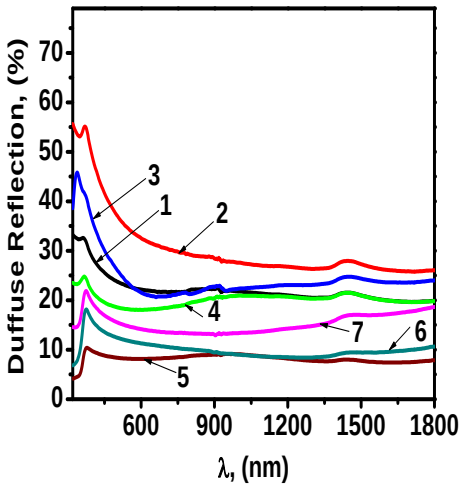

Figure 7. Spectra of diffuse reflection of: 1 – as-cut multi-Si substrate, 2 – plasma etched multi-Si substrate, 3 – ZnO deposited on plasma etched multi-Si with 8 nm Ag seeding layer for 60 min, 4 – ZnO deposited on as-cut multi-Si for 90 min, 5 – ZnO deposited on plasma etched multi-Si for 30 min, 6 – ZnO deposited on plasma etched multi-Si for 60 min, 7 – ZnO deposited on plasma etched multi-Si for 120 min.

Si substrates has been observed (Fig.7, curve 1). It can be assumed in this case that Ag layer contributes in the additional reflection from this structure EDS analysis shows that the deposited films consist of ZnO. More detailed analysis of the composition of the ZnO based layer (including depth resolved dependencies) is required. Such analysis is a subject for further studies of the ZnO based structures presented in this work.

3.5. Diffuse reflection of ZnO grown on Cu thin plate Diffuse reflectance spectra of ZnO films grown on top of the Cu thin plate substrates are shown in Fig. 8a. All spectra have been recorded in the spectral range of 350 – 1800 nm. The corresponding spectrum of the pure Cu plate is shown, as well, for a comparison. Fig.8b shows direct reflection spectra of the same samples. From Fig 8 it can be seen that in the whole spectral region under investigation the diffuse reflection of the pure Cu plate is much lower than the direct reflection of the same Cu plate. Absolute values of the diffused reflection of the electrochemically deposited ZnO layers are close to values of the direct reflection for the same ZnO/Cu structures. From Fig. 8a it can be seen that an increase of the electrochemical deposition time of the ZnO layers results in an increase of the diffused reflectance values due to the changes of the surface morphology. Indeed, formation of higher and thicker nanowalls can be seen from the SEM images, taken for ZnO/Cu structures processed for 90 and 120 min. It is necessary to note that the absolute value of the diffused reflection depends on a number of parameters of the ZnO based structures grown on Cu substrates. The following parameters of the ZnO nano-structures can be mentioned in this regard - the size and the shape of the nanowires and nanowalls, the surface roughness of the deposited films, the refractive index, etc. Further detailed studies are required to explain the observed experimental results, which show that ZnO based structures deposited on Cu substrates exhibit rather strong reflection created by a ZnO/Cu mirror, which reflects light in the wide range of the spectrum. It has to be noted that such reflection can be potentially utilized for the thin Si solar cell fabricated on top of such mirror-like ZnO/Cu based structures.

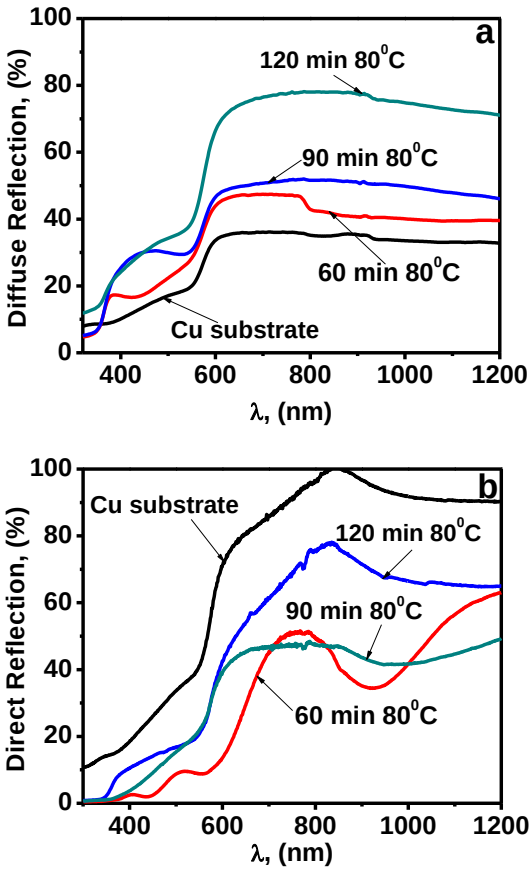

Figure 8. Spectra of diffuse (a) and direct reflection (b) of ZnO thin layers deposited on Cu plate for different times: 60, 90 and 120 min. The corresponding spectra for a pure Cu plate are presented as well.

Conclusion It is demonstrated that ZnO layers grown by electrochemical deposition on different highly conductive substrates (Si, Cu) have different morphologies**.** It is observed that ZnO nanorods with hexagonal shape can be formed on multi-Si substrate etched by an Ar^+ plasma.

It is shown that in some cases (30 minutes deposition on etched Si substrate) ZnO based NRs deposited on Si substrates provide formation of an antireflection coating (ARC, reflection < 10%), which can be used for Si based solar cells. Although further optimization of such ZnO NRs based structures are required, the obtained result can be considered as a promising technological development towards low-temperature and cost effective non-vacuum technology for the processing of ARCs for Si based as well as other types of solar cells.

It is shown that deposition of ZnO based structures on Cu thin plate substrates leads to the formation of ZnO based nanowalls. An increase of the diffused reflection with the increase of the deposition time is observed.

It can be assumed that that such mirror-like ZnO/Cu based structures with an enhanced diffuse reflection can be utilized for the thin Si solar cell fabricated on top of such structures. Further investigations targeting processing of solar cells (like thin film a-Si:H based) on top of ZnO/Cu substrates fabricated using the proposed approach are required to clarify this point.

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