Dependence of the optical and structural properties of ZnO:Al nanostructured layers deposited electrochemically on seeding multilayer stack substrates

M Petrov¹, K Lovchinov, M Ganchev, O Angelov, H Nichev and D Dimova-Malinovska

Central Laboratory of Solar Energy and New Energy Sources,
Bulgarian Academy of Sciences, 72 Tsarigradsko Chaussee, 1784 Sofia, Bulgaria

E-mail: petrov80@abv.bg

Abstract. We report studies on the optical and structural properties of nanostructured ZnO layers doped with Al (ZnO NW) electrochemically grown on conductive substrates, namely, ZnO:Al/Ag/ZnO:Al multilayer stack structures deposited on glass substrates. Multilayer transparent conductive stack structures with different thickness of the middle Ag film (10 nm, 16 nm and 20 nm) with plasmonic properties were prepared by magnetron sputtering of ZnO:Al and Ag targets. Additionally, a seeding stack annealed at 180 °C for 50 min was prepared in order to study the influence of the seeding stacks properties – resistivity and structure, on the optical and structural characteristics of the electrochemically-grown ZnO layers. A correlation was observed between the surface roughness and the diffuse reflection and the haze ratio in reflection. The results are discussed in terms of the influence of the size of the Ag grains and their distribution in the middle Ag film in the seeding stacks on the nucleation and growth of ZnO NW. The ZnO NW layers exhibited higher values of the diffuse reflection in the 400 – 1100 nm spectral range; they can be applied as rear contacts of thin films solar cells thus increasing the light trapping.

1. Introduction

ZnO is recognized as one of the most promising semiconductor oxide materials due to its good optical, electric and piezoelectric properties. This has prompted a growing interest in its application in solar cells, photonic devices, including laser and light-emitting diodes with low thresholds, optical waveguides and optical switches, sensors, field emission sources and displays [1-4]. Different methods of fabrication of ZnO nanostructured layers have been developed – electrochemical deposition, sol-gel preparation, sputtering deposition, aqueous chemical growth etc. Additionally, noble metal nanoparticles with plasmonic properties are of great interest for application as back reflectors for increasing the light trapping in thin-film solar cells [5, 6]. Nanostructured ZnO films used as electrodes have demonstrated appropriate surface morphology for high light-trapping and optical confinement in thin-film solar cells with increased efficiency [5]. Recently, fabrication was reported of conductive multilayer stack structures with increased diffuse reflection and plasmonic properties in the

¹To whom any correspondence should be addressed.
visible and IR region on the basis of Al doped ZnO (ZnO:Al) films and Ag nano-particles deposited by magnetron sputtering [5-7].

In this paper we report results from the study of the structural and optical properties of ZnO nano-structured films grown by electrochemical deposition on glass substrates coated by seeding conductive multilayer stack ZnO:Al/Ag/ZnO:Al structures. Studies of the surface structure by SEM and AFM demonstrated changes in the surface morphology and roughness of the electrochemically-deposited ZnO layers as the thickness of the Ag film in the stack structures was varied. A correlation was observed between the diffuse reflection and the haze ratio in reflection.

2. Experimental
ZnO nanostructured films were deposited by means of an electrochemical process from aqueous acid solutions of ZnCl$_2$ ($5 \times 10^{-3}$ M) and KCl (0.1 M) with pH 6.5 at a temperature of 60 °C using a three-electrode electrochemical cell with a saturated calomel electrode (SCE) as a reference electrode. Stöke solution of $4 \times 10^{-5}$ M Al$_2$(SO$_4$)$_3$ was added to the electrolyte to deposit Al-doped ZnO layers. The deposition process of ZnO was carried out at $-1.0$ V vs. the SCE preventing a metal Zn deposition. ZnO films of good quality were obtained at a redox potential within the range between $+0.30$ V and $+0.40$ V vs. the SCE. Zinc peroxide (ZnO$_2$) was formed on the samples with bad adhesion to the substrate at a redox potential higher than $+0.40$ V. A spectrally-pure graphite plate electrode was used as an anode. The electrolyte was agitated by a magnetic stirrer. The deposition time was 15 min. The substrates used consisted of glass coated by three-layer stack structures – glass/ZnO:Al(20 nm)/Ag(x nm)/ZnO:Al(20 nm). The thickness of the middle Ag film in the seeding stack structures, x, was varied as follows: 10 nm (substrate S3), 16 nm (substrate S2) and 20 nm (substrates S1 and S4). To compare the properties of the electrochemically deposited ZnO layers on as-deposited (S1) and annealed seeding stacks, a structure (S4) with a Ag thickness of 20 nm was fabricated after annealing the first two layers ZnO(20 nm)/Ag(20 nm) at 180 °C for 50 min followed by deposition of the capping ZnO (20 nm) film.

The surface morphology of the deposited films was studied by a scanning electron microscope (SEM) Philips 515. The AFM analysis was performed by an NT-MDT Solver 47 Pro system in a “semi-contact” (tapping) mode and the root-mean-square (rms) roughness was calculated by the Gwyddion software. The optical spectra were obtained by a Shimadzu UV-3600 spectrophotometer in the 320 – 1200 nm range employing a 60-mm integrating sphere for diffuse transmission and reflection spectra measurements. The resistivity of the seeding stack structures was measured by the four-point probe method using a VEECO apparatus.

3. Results and discussion
Some characteristics of the seeding stack structures and of the ZnO layers deposited electrochemically on them is given in table 1. The stack structures’ resistivity increases with the decrease of the thickness

Table 1. List of the substrate structures and of the electrochemically deposited ZnO NW layers, the thickness of the middle Ag films, x, resistivity of the stack structures, ρ, the root-mean-square roughness of the seeding stakes structure, rms, and of the ZnO NW layers, RMS, the haze ratio in reflection of the stack structures, $h_R$, and of the ZnO NW, $H_R$, at two wavelengths – 400 nm and 1000 nm.

| ZnONW samples | Stack structures | x, (nm) | ρ, (Ω·cm) | rms (nm) | RMS (nm) | $h_R$(% 400 nm) | $H_R$(% 400 nm) | $h_R$(% 1000 nm) | $H_R$(% 1000 nm) |
|--------------|------------------|--------|-----------|----------|----------|----------------|----------------|----------------|----------------|
| 1            | 1S               | 20     | $33 \times 10^3$ | 9        | 95       | 20             | 91             | 15             | 35             |
| 2            | 2S               | 16     | $1.0 \times 10^4$ | 4        | 106      | 20             | 94             | 14             | 32             |
| 3            | 3S               | 10     | $1.0 \times 10^4$ | 6        | 330      | 21             | 85             | 17             | 25             |
| 4            | 4S (annealed 1S) | 20     | $23 \times 10^3$ | 10       | 85       | 28             | 50             | 38             | 13             |
of the middle Ag film in the seeding stacks from 20 nm to 10 nm. Annealing the two-layer structure with a 20-nm Ag film at 180 °C for 50 min before capping with the upper ZnO (20 nm) results in an increase of the resistivity of the three-layer stack to $2.3 \times 10^{-1}$ Ω cm. Similar dependence has been reported by other authors, e.g. [6].

The higher conductivity can be explained by the increased thickness of the middle Ag layer and the formation of a chain area, as seen from the TEM and SEM analyses published in [7]. Thus, the barrier height between the grains decreases and the mechanism of conductivity of the layer changes from thermally activated hopping to a metallic-type one [8]. After annealing the as-deposited stack with a 20-nm thick Ag film, the island-like areas split and the Ag nano-grains separate, which leads to a rise in the structure’s resistivity. The surface roughness value slightly decreases as the thickness of the Ag film is decreased and does not change significantly after annealing.

Figure 1 shows SEM micrographs of electrochemically-deposited ZnO layers. It is seen that these layers consist of nano-whiskers (ZnO NWs). Their thickness and length increase from about 100 nm to 200 nm and from 1 µm to 3 µm, respectively, while their density decreases as the thickness of the middle Ag films in the seeding stack structures is raised. The electrochemically-deposited ZnO layer on the annealed stack structure exhibits NWs that are smaller in size and distributed more tightly than those on the as-deposited seeding stack.

**Figure 1.** SEM micrographs of the electrochemically-deposited ZnO NW layers on different stack structures: (a) $x = 10$ nm, sample 3 on seeding stack 3S, (b) $x = 16$ nm, sample 2 on seeding stack 2S, (c) $x = 20$ nm, sample 1 on seeding stack 1S and (d) $x = 20$, sample 4 on seeding stack 4S (annealed). The markers correspond to 1 µm.

One should note that the diverse structures of the seeding layers with different resistance lead to different currents and inhomogeneity in the cathode field. This results in different growing speed and different morphology during the electrochemical deposition of the films. The changes in the RMS values are due to the different surface morphology of the ZnO NWs layers.

Figure 2 displays AFM images of the ZnO NW layers. It is seen that the rms values of the roughness of the seeding stacks are low (in the range 4 – 9 nm) and 10 nm in the annealed stack. The RMS roughness of the ZnO NWs layers is much higher and decrease from 330 nm to 93 nm with the
increase of the Ag film thickness in the seeding stacks from 10 nm to 20 nm. The roughness of the ZnO deposited on the annealed stack \( x = 20 \) nm (sample 1) is the lowest (85 nm), which is probably related to the formation of separated Ag particles in the seeding stack and the resulting smaller size and tighter distribution of the grown NW.

The optical transmittance (a), reflectance (b), diffuse transmission (c) and reflection (d) spectra, and the haze ratio in transmission (e) and in reflection (f) of the ZnO NW layers deposited on different seeding stack structures (solid curves) are shown in figure 3. For comparison, the corresponding spectra of the seeding stack structures are presented as well (dashed curves). The presence is clearly seen of absorption and reflection plasmonic bands in the spectra of the seeding stack structures. The band at about 365 nm corresponds to the quadrupolar resonance and the near lying inter-band electron transitions in the entirely filled electron d-shell of the Ag atoms [8]. The position of the other band at about 460 nm due to the plasmon resonance in the Ag nano-grains is red-shifted as the thickness of the middle Ag film and the Ag grain size in it rise. The stacks deposited with Ag layers of 16 nm and 20 nm, which have a higher conductivity, demonstrate a plasmon absorption due to the free-carrier absorption in the IR region (figure 3a). As the thickness of the middle Ag layer in the stack structures is reduced (and its resistivity rises), the transmittance of the samples in the IR region increases, as is very clearly pronounced in the annealed-stack case (figure 3d). The same bands of absorption and reflection due to the plasmon effect are observed in the electrochemically-deposited ZnO layers, albeit

![Figure 3](image_url)

**Figure 3.** Spectra of optical transmittance (a), reflectance (b), diffuse transmission (c) and reflection (d), haze ratio in transmission (e) and in reflection (f) of the ZnO nanostructured layers (solid curves) deposited on different seeding stack structures: sample 1, \( x = 20 \) nm on seeding stack 1S, sample 2, \( x = 16 \) nm on seeding stack 2S, sample 3, \( x = 10 \) nm on seeding stack 3S and sample 4, \( x = 20 \) nm on seeding stack 4S (annealed); the corresponding spectra of the seeding stack structures (dashed curves) are shown for comparison.
less well pronounced. The ZnO NW layers grown electrochemically on as-deposited stack substrates possess lower transmittance (figure 3a) and reflectance (figure 3b) values. However, they have lower reflectance and higher diffuse transmission and reflection values (figure 3c and d) than those of the seeding stack. The haze ratios in transmission (figure 3e) and in reflection (figure 3d) are much higher than those of the seeding stack structures, which corresponds with their higher RMS surface roughness (table 1). The haze in transmission and reflection depends weakly on the thickness of the middle Ag film in the seeding stacks for x = 20 nm and x = 16 nm. The diffuse reflectance values are > 40 % for wavelengths λ < 800 nm, and 85 – 90 % at λ = 400 nm, in the case of ZnO NW grown on the as-deposited stack structures. Only in the case of deposition on the annealed seeding stack are the diffuse transmission and reflection and the corresponding haze ratio lower, probably due to the denser distribution of the NW in the grown layers and the lower RMS roughness, (RMS = 85). The ZnO layer deposited electrochemically on ZnO/Ag/ZnO stacks have higher values of the diffuse reflection and the haze ratio in reflectance in the visible range of the spectra, as compared to those of the seeding stacks. This correlates with the values of the surface roughness.

4. Conclusions
The study of nanostructured ZnO layers with nano-wiskers deposited electrochemically on multilayer ZnO:Al/Ag/ZnO:Al stack structures demonstrated that the optical and structural properties of the grown ZnO NW layers depend on the properties of the seeding multilayer stack structures. Changing the thickness of the middle Ag film and annealing the stack structure result in changes of its structural and electrical properties. The size of the nano-grains in the middle Ag film of the seeding stack affects the NW ZnO layers growth – it determines the size of the nano-whiskers and the surface roughness in the nanostructured ZnO layers as well. The stack structures exhibit a plasmonic effect due to the presence of Ag nano-grains. Plasmonic properties of the grown ZnO NW are also observed, although less well pronounced than in the seeding stack structures. The electrochemically-deposited ZnO layers demonstrate very high values of the diffuse reflection and the haze ratio in reflection in the visible and near IR spectral ranges. ZnO layers having a larger size of the nano-whiskers and higher values of RMS roughness are grown on the stack structure with a 20-nm thick Ag film, which includes Ag nano-grains connected in chains and has a higher conductivity. They demonstrate higher values of the diffuse reflection and of the haze ratio in reflection in the spectral range of 400 nm – 1100 nm. The metal nanoparticles in the seeding stacks, together with the nano-wiskers in the electrochemically-grown ZnO, could enhance the scattering of the light in the solar cells in the visible and near IR spectral ranges. The nanostructured ZnO layers possessing a higher diffuse reflection, an increased effective area, a higher surface roughness and plasmonic properties can be applied as rear contacts in thin-film solar cells with improved light-harvesting properties.

Acknowledgements
This work supported by the 7 European FP under project NanoPV No. 24331 and by the Bulgarian National Science Fund under project No. 859/2012.

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