



Formation of Hierarchical Zinc Oxide Nanostructures for Solar Energy Converters and Photovoltaics

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Abstract. Zinc oxide is a promising material for the fabrication of thin film layers for a new generation of photovoltaic devices and solar thermal collectors, due to the unique optical and electrical properties as well as the propensity to form filamentous one-dimensional submicron structures, namely nanowires, nanorods, nanotubes, nanobelts, and hierarchical nanostructures with developed surface and projected superhydrophobicity. We identified the possibility for a development of planar single-layer antireflection coatings and/or arrays of nanorods of this material as having the shape of hexagonal prisms, and demonstrating the moth eye effect on the substrates of transparent conductive tin dioxide and on silicon wafers with embedded homojunctions. The optimization of the pulsed electrodeposition of zinc oxide arrays adjust the size of parabolic nanonipples for the implementation of antireflection coatings with the moth eye effect on various substrates, including flexible. The antireflection coatings will be developed for thin-film photovoltaic devices of substrate configuration based on kesterite, tin sulphide, and fullerene layers, for the cadmium telluride based photovoltaic cells with bilateral sensitivity of superstrate configuration on the flexible substrates and for optoelectronic devices based on zinc selenide for the ultraviolet spectra.

Keywords. formation, nanostructures, zinc oxide, solar energy, converters, photovoltaics

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Introduction

Zinc oxide is a promising wide-gap material, which has the ability to achieve high concentrations of intrinsic defects (oxygen vacancies and interstitial zinc atoms), which allows to vary the optical properties, conductivity of the medium, and luminescent characteristics.

Recently, in theoretical studies and in practice, there has been an increased interest in multi-layer systems incorporating p/n -ZnO structures, which is due to their possible practical application as high-transparency electrical contacts and buffer layers in thin-film solar cells (Deo et al., 2012; Jiang et al., 2013; Kang et al., 2015; Kennedy et al., 2014; Musselman et al., 2011; Rahmani et al., 2017; Sathyaseelan et al., 2016). Thus, the actual task is to develop a technology for the production of crystalline film p/n -ZnO

structures with a variable concentration of intrinsic defects. In particular, it is interesting to develop layered systems for thin-film transducers in the formation of A2B6 films between p/n -ZnO layers.

The aim of this work is obtaining hierarchical structures of ZnSe/ZnO and to study their properties.

Experimental Procedure

Zinc selenide films were obtained by electrochemical sintering from alkaline electrolytes: zinc layers from an alkaline galvanizing electrolyte preliminarily deposited on a metal substrate. Then, the zinc substrate was selenated in the electrolyte of the following composition: 1–3

M solution of NaOH, 0.5M Se. The selenification temperature is 80°C, the selenium time is 5–40 minutes. The cathode current density was varied in the range 50–150 mA/cm². The ZnO film on the surface of ZnSe layers was formed by oxylation of zinc selenide in air. The oxidation temperature was varied in the range 300–400°C, the duration of oxidation was up to 1 h.

Results and Discussion

The formation of zinc selenide on the surface of the electrode was confirmed by the results of X-ray diffraction analysis: reflection reflections were observed in the diffractograms, which can be attributed to the sphalerite modification of zinc selenide. From the 1M solution at a low cathode current density (50 mA/cm²), films formed by spherical-shaped agglomerates with dimensions of 0.5–1.2 µm were formed. With increasing cathode current density and selenium time, a decrease in the size of the agglomerates (less than 100 nm) was observed. With an increase in the concentration of alkali and low current densities, an increase in spherical agglomerates to 2 µm was observed (Figures 1 and 2). An increase in the current density and the time of selenium in the 3M NaOH solution led to the formation of a film in the form of individual agglomerates with dimensions up to 5 µm (Figure 1d and Figure 2d).

The thickness of the films (Figure 3) increased with increasing deposition time and current density, reaching 5 (1M NaOH, 150 mA/cm²) and 10.5 µm (3M NaOH, 150 mA/cm²). Two sections of the curve were distinguished on the curves: on the first, there was an intensive growth of the film thickness (deposition up to 10 min at $j_k = 0.05$ A/cm² and up to 20 min at $j_k = 0.15$ A/cm²); on the second, the growth of the film thickness was significantly slowed down.

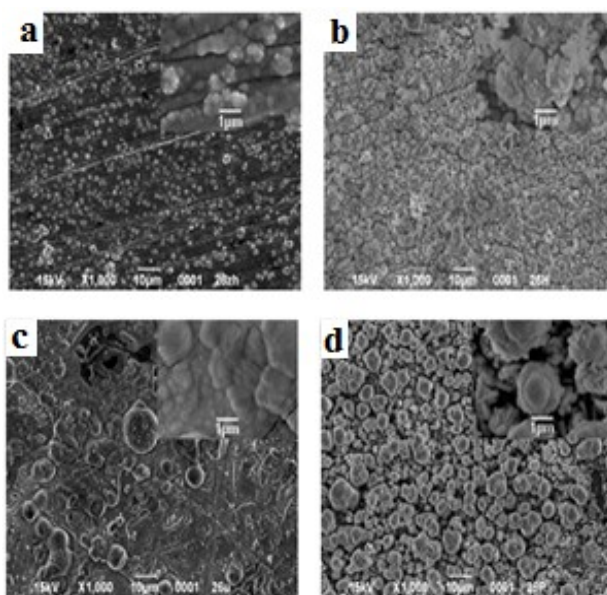


Figure 1: Microphotographs of zinc selenide films obtained in a 2M NaOH solution at a current density (mA/cm²) and seleniding time (min), respectively: a) 50 mA/cm², 15 min; b) 150 mA/cm², 15 min; c) 50 mA/cm², 60 min; d) 150 mA/cm², 60 min

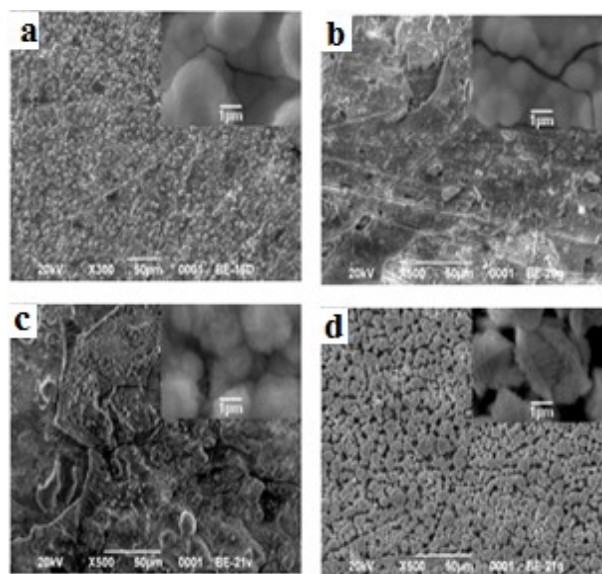


Figure 2: Microphotographs of zinc selenide films obtained in 3M NaOH solution at current density (mA/cm²) and seleniding time (min), respectively: a) 50 mA/cm², 15 min; b) 150 mA/cm², 15 min; c) 50 mA/cm², 60 min; d) 150 mA/cm², 60 min.

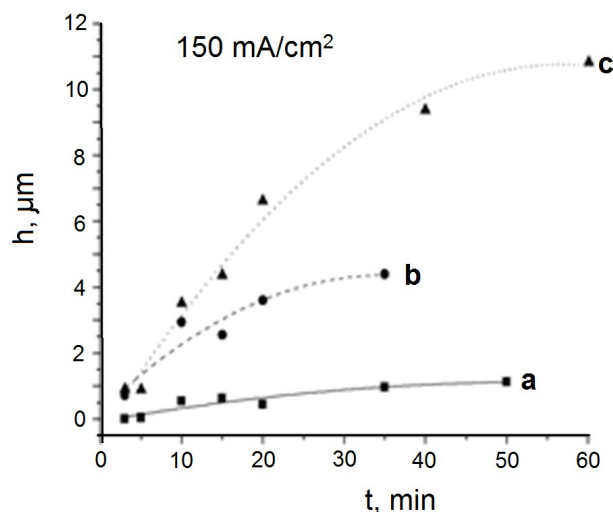


Figure 3: Dependence of film thickness on deposition time at 150 mA/cm^2 current density and a concentration of NaOH of 1 mol/L (a), 2 mol/L (b) and 3 mol/L (c)

This slowing of the growth of the film was associated with an increasing difficulty in the diffusion of selenide ions through the growing film. An analysis of the polarity of thermo-emf showed that all films had a *p*-type conductivity. Irrespective of the conditions of selenium, the resistivity of the films varied between 105 and 106 Ohm·m.

Zinc oxide films were formed by oxidation of zinc selenide by heating in air. The oxidation regime was chosen so that the part of the film of selenide adhering to the metal substrate retained its structure and phase composition, and the oxidation occurred only on the surface of the film. The formation of zinc oxide was confirmed by IR spectrometry (Figure 4). In the IR spectra of films annealed at temperatures above 300°C , an absorption band of 422 cm^{-1} was observed, which is associated with vibrations of the Zn–O group.

The dark volt-ampere characteristic of the synthesized ZnSe/ZnO heterosystem is shown in Figure 5. The asymmetry of the current-voltage characteristic indicates that as a result of oxidation of the surface of the zinc selenide film in the interphase boundary region, a *p-n* junction was formed that effectively separates the light-excited charge carriers, ensuring the functioning of the system as a photoconverter.

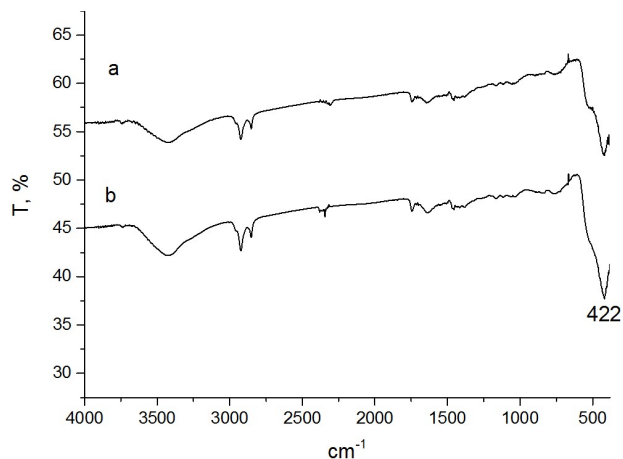


Figure 4: IR spectrum after annealing at 350°C (a) and 400°C (b) for 30 and 7 minutes, respectively.

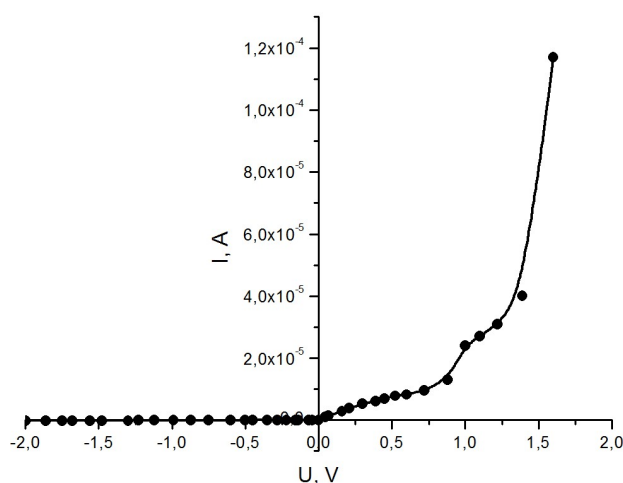


Figure 5: Volt-ampere characteristic of synthesized ZnSe/ZnO heterosystem.

Conclusions

The following ways to improve the results of these studies are by developing the design of multilayer selective coatings for the solar thermal collectors with record optical properties in which the selectivity will be improved by the use of zinc oxide arrays. The combination of the anti-reflection properties of the surface with its self-cleaning properties is particularly important in the operation of solar power products with large areas and will have a major economic effect.

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