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# Nanostructured solar cell based on spray pyrolysis deposited ZnO nanorod array

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ABSTRACT

In this paper we present a realization of an extremely thin absorber (ETA) layer solar cell by the chemical spray pyrolysis method. $CuInS_2$ absorber was deposited onto a blocking layer coated ZnO nanorods grown on a transparent conductive oxide. Layers and cells were characterized by optical and Raman spectroscopy, and scanning electron microscopy. Current–voltage, spectral response and electron beam induced current measurements were applied to solar cells. ZnO nanorod cell showed twice higher short circuit current density than the flat reference. ETA cells with efficiency of 2.2% ($j = 12\,mA/cm^2$, $V_{oc} = 425\,mV$, FF = 43%) and of 2.5% were prepared using $TiO_2$-anatase and an indium sulfide blocking layer, respectively.



## 1. Introduction

Low-cost deposition techniques and new designs are of continuous interest to reduce production costs of photovoltaic devices. In recent years, nanostructure use in photovoltaic devices has attracted major interest. Dye sensitized photoelectrochemical solar cell (DSSC) based on nanoporous titanium dioxide is the best-known representative of the family of nanostructured PV devices [1]. Stability problems of DSSC, including its solid-state modifications, promote development of the concept of extremely thin absorber (ETA) cell which uses an extra thin absorber sandwiched between two strongly interpenetrating transparent wide bandgap semiconductors [2]. $TiO_2$ is the most frequently used n-type nanostructured window material in the ETA cell. As an alternative, nanostructured columnar zinc oxide has been used to prepare ZnO/CdTe ETA cell [3]. Inorganic absorber materials like CdTe [3,4] and CdSe [5–7] have been used in nanostructured ZnO based cells. The conversion efficiency of 2.3% has been achieved in ZnO nanowire based ETA cells [5,6]. ZnO nanowire layers for photovoltaic application have been fabricated by electrodeposition [3–7], metal organic vapour deposition [8] and hydrothermal growth [9].

Recently a low-cost deposition route to grow ZnO nanorod arrays on conductive transparent electrodes by chemical spray was developed by our group [10–12]. In this study, we describe the preparation and properties of solar cells based on nanostructured layers comprising ZnO nanorods and copper–indium disulfide absorber layer. Both ZnO nanorods and the absorber layer were deposited by the chemical spray pyrolysis method.

## 2. Experimental

ZnO nanorods were deposited by spray of zinc chloride aqueous solutions onto the indium tin oxide (ITO) covered glass substrates at deposition temperatures slightly above 500 °C. ZnO nanorod layer ($ZnO_R$) deposition by the spray technique is reported in detail in our previous studies [10–12]. To prepare a ZnO structured layer based solar cell, the following layers were deposited by keeping the sequence: $ZnO_R$, $TiO_2$ or 'InS' blocking layer, $In_2S_3$ and finally, $CuInS_2$ (CIS). A thin film of $TiO_2$ as a blocking layer was prepared by the sol–gel dip coating method using the titanium tetra-isopropoxide based titania sol [13]. As an alternative, a dense layer of indium sulfide was used instead of a $TiO_2$ blocking layer. This layer (named 'InS') was deposited by spray using the solution containing $InCl_3$ and thiocarbamide ($SC(NH_2)_2$) in a molar ratio of In:S = 1:3 at pH~5. Indium sulfide ($In_2S_3$) buffer layer was deposited by spray using the spray solution of $InCl_3$ and $SC(NH_2)_2$ with the molar ratio of In:S = 1:3 at $InCl_3$ concentration of $2 \times 10^{-3}$ mol/l and pH~3. $CuInS_2$ (CIS) absorber layer was deposited by spray using the solution containing $InCl_3$, $CuCl_2$ and $SC(NH_2)_2$ at the molar ratios of Cu:In:S = 1:1:3, following the preparation route described elsewhere [14]. Indium sulfide layers and CIS absorber layer were grown at a similar temperature close to 300 °C. Flat solar cells (no ZnO rods) as reference samples were prepared simultaneously with the structured cells. Component layers were identified by their bandgap ($E_g$) or Raman spectra. The optical transmittance

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and reflectance spectra of the component layers and the structures were measured in the wavelength range of 200–2500 nm at room temperature on a Jasco V-670 UV–VIS–NIR spectrophotometer fitted with an integrating sphere. Raman spectra of the layers were recorded in the backscattering nonpolarized mode at room temperature using a confocal laser micro-Raman spectrometer HORIBA Jobin Yvon Model HR 800. The excitation radiation wavelength was 532.0 nm and the intensity was $10^7$ W/m$^2$.

Surface morphology and cross-section views of the structures were examined by high-resolution scanning electron microscopy (SEM) on Zeiss HR FESEM Ultra 55. The image of p–n junction was investigated with the help of electron beam induced current (EBIC) detector. Photoconversion of the solar cells was characterized by *I–V* curves in the dark and under the halogen lamp illumination (intensity 100 mW/cm$^2$). External quantum efficiency (EQE) spectrum of the solar cells was measured in the wavelength range of 400–1200 nm using 100 W halogen tungsten quartz (HTQ) lamp and SPM-2 monochromator ($f = 40$ cm). Graphite was used to make electrical contacts.

## 3. Results and discussion

### 3.1. Choice and characterization of solar cell component layers

In this study we prepared solar cell onto the spray deposited nanostructured ZnO layers comprising elongated crystals. SEM cross-sectional micrograph of the ZnO nanorod layer on ITO electrode is presented in Fig. 1a. $TiO_2$ blocking layer was deposited onto the structured zinc oxide to protect ZnO from dissolution during the deposition of acidic solution to form $In_2S_3$ buffer and copper indium disulfide absorber layers. Another role of $TiO_2$ blocking layer was to avoid electrical short-circuiting of the solar cell structure. In previous studies, a continuous ZnO or $TiO_2$ layer has been deposited first on the conducting transparent electrode to avoid any contact and consequent short-circuiting between the front and back contact [4,5,7,15] and ZnO rods were grown on those metal oxide layers.

Fig. 2 shows Raman spectrum of the flat $TiO_2$ film as a reference sample prepared in parallel to depositing $TiO_2$ onto the structured ZnO layer. Raman peaks at 144, 196, 398, 518 and 638 cm$^{-1}$ confirm the formation of $TiO_2$–anatase film [16].

An alternative blocking layer, 'InS', was deposited by spray in order to reduce the preparation time, to keep spray process continuous and thus to simplify the solar cell fabrication process. According to the SEM study (SEM microphoto is not presented), thin, dense and pinhole-free 'InS' film was formed. Both indium sulfide films, 'InS' blocking layer and $In_2S_3$ buffer layer, show a similar band gap value of 2.0 eV (Fig. 3). The bandgap of indium sulfide films was calculated from the optical transmittance and reflectance spectra, assuming the indirect transition type and linearity of $(\alpha h\nu)^{1/2}$ vs. $h\nu$ plot.

The sequence of component layers in the solar cells based on nanostructured ZnO and their flat references together with cell numbering is as follows:

1. ITO/$TiO_2$/$In_2S_3$/CIS (flat);
2. ITO/$ZnO_R$/$TiO_2$/$In_2S_3$/CIS (structured);
3. ITO/'InS'/$In_2S_3$/CIS (flat);
4. ITO/$ZnO_R$/'InS'/$In_2S_3$/CIS (structured).

SEM cross-sectional microphoto of ITO/$ZnO_R$/$TiO_2$/$In_2S_3$/CIS structure (cell 2) is presented in Fig. 1b. As can be seen, ZnO crystals in the solar cell structure are covered with a CIS layer with

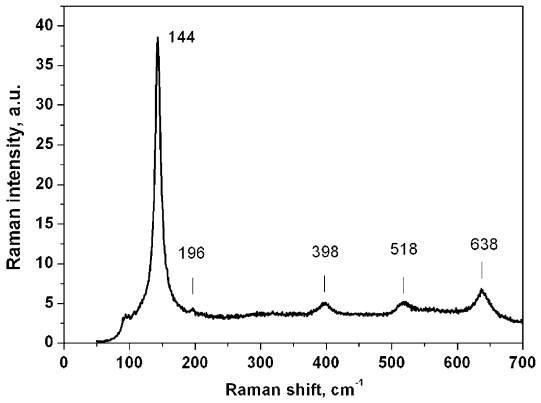


**Fig. 2.** Raman spectrum of the $TiO_2$ film made by sol–gel dip coating on a glass substrate and annealed for 30 min at 450 °C in air.

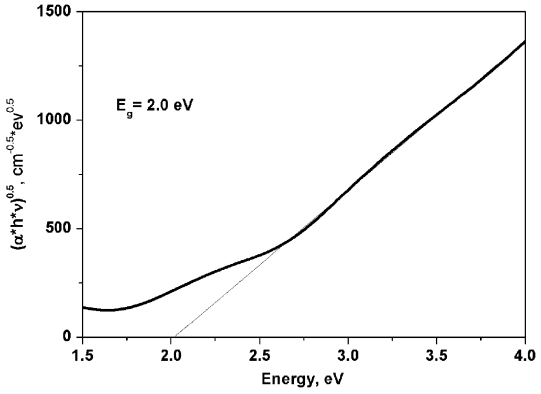


**Fig. 3.** Determination of the optical bandgap of the spray deposited indium sulfide buffer layer.

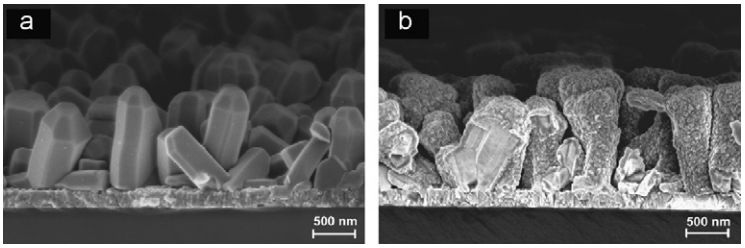


**Fig. 1.** SEM cross-sections of spray deposited ZnO nanostructured layer on indium tin oxide (ITO) covered glass substrate (a), and the solar cell structure (ITO/$ZnO_R$/$TiO_2$/$In_2S_3$/CIS) before conducting (b).