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Nanostructured solar cell by spray pyrolysis: Effect of titania barrier layer on the cell performance

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ABSTRACT

ZnO nanostructured solar cells with $CuInS_2$ absorber layer were prepared by chemical spray method. In order to increase chemical stability of ZnO nanorods against dissolution in the next steps of the cell preparation, and reduce the electrical shorts between the front and back contacts, an amorphous TiO_2 layer was deposited on ZnO nanorods by ALD or sol–gel spray technique. The thicknesses of the layer (≤5 nm by spray and ≤1 nm by ALD), which did not impede the collection of carriers, were determined. TiO_2 thicknesses above these optimal values led to s-shaped *I–V* curves, causing the decrease in solar cell efficiency from 2.2 to 0.7% due to the formation of an additional junction blocking charge carrier transport in the device under forward bias. Nanostructured cells suffered from somewhat higher interface recombination but showed still two times higher current densities (~10 mA/cm^2) than the planar devices did.

1. Introduction

Zinc oxide nanowire arrays are promising building blocks for nanostructured solar cells such as dye-sensitized (DSC) and extremely thin absorber (ETA) layer solar cells [1]. Although ZnO nanorod arrays can be manufactured by different gaseous or solution based techniques, layers made by solution based techniques such as electrodeposition and chemical bath deposition have mainly been used for ETA cells so far [2–5]. The best conversion efficiencies of 2.3% and 2.5% have been reported for this kind of cells using CdSe or In_2S_3, respectively, as an absorber layer [4,5].

Recently we showed that ZnO rods could be grown also by a simple spray pyrolysis method [6,7]. A structured solar cell based on a ZnO nanorod array and $CuInS_2$ absorber layer, both prepared by spray technique, demonstrated the conversion efficiency of 2.5% [8]. In this cell, ZnO rods were directly grown onto the conductive electrode and a thin layer of TiO_2 was deposited on the top of the ZnO nanorod array by dip coating to form so-called ZnO/TiO_2 core shells. It has been reported that deposition of interfacial blocking layers such as ultra-thin Al_2O_3 on nanoporous TiO_2 or a thin TiO_2 layer on ZnO nanowires improves the output parameters of DSC via suppression of interfacial recombination [9,10]. In this application, the thickness and crystallinity of the shell both have crucial effect on the cell output characteristics [10,11].

Thin metal oxide shells on nanostructures were mainly deposited by atomic layer deposition (ALD) technique [10,12]. The ALD processes are based on self-saturating surface reactions and for this reason, films of uniform thickness can successfully be obtained even on profiled substrates as demonstrated e.g. by coating the walls of trenches with the width of about 100 nm and depth to width ratio of 40 [13]. At the same time the thickness of the films deposited by this method can be controlled very precisely as less than one atomic layer of the film material is usually deposited in each reaction step the ALD process is consisted of. However, a simple and low-cost dip coating method has also been used for the deposition of oxide shells on nanostructured surfaces [8,14,15].

In the present study, thin layers of TiO_2 were deposited onto ZnO nanocolumns to protect the columns from dissolution when acidic solutions were used in the next manufacturing steps of the solar cell. The layers were prepared by sol–gel spray and ALD methods and the effect of the deposition method and layer thickness on solar cell output characteristics was studied in order to determine optimal conditions for the barrier layer preparation.

2. Experimental

Structured ZnO layers (ZnO_{STR}) composed of nanocolumns with diameters of 200–300 nm and lengths of ~500 nm were deposited by the chemical spray method onto indium tin oxide (ITO) covered glass substrates using $ZnCl_2$ as a zinc source as reported elsewhere [6,7,16]. A scanning electron microscopy (SEM) micrograph of a ZnO layer is shown in Fig. 1a. In order to improve the carriers collection in the structure, a thin layer of ZnO:In was deposited on the ZnO_{STR} layer using Zn-acetate solution with $InCl_3$ as a dopant salt (In/Zn=3 at.%) and deposition conditions described earlier [17].

The next layer of the solar cell structure is TiO_2, which was deposited by ALD or sol–gel spray methods. ALD of TiO_2 was performed in

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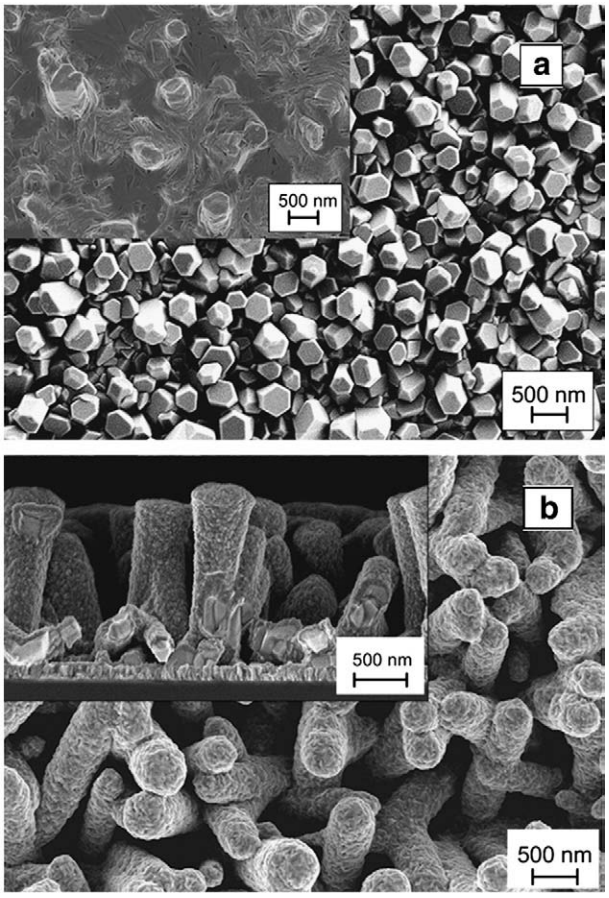

Fig. 1. SEM micrographs of (a) ZnO nanocolumnar layer before and after (inset) spraying on that acidic (pH ~2.8) solution and (b) ZnO nanorod array with a thin TiO_2 layer (50 ALD cycles) after spraying of $CuInS_2$ layer using acidic solution.

a low-pressure flow-type reactor [18] at a substrate temperature of 200 °C. The ALD process consisted of cycles including exposure to titanium tetraisopropoxide (TTIP), purge in pure N_2, exposure to H_2O and another purge with N_2. The number of cycles applied in a growth run was varied from 40 to 275. According to high-energy electron diffraction studies performed for samples with Si substrates, these process parameters yielded predominantly amorphous TiO_2 films. Only the thicker films i.e. those grown by applying 200–275 cycles, showed minor traces of the anatase phase. The dependence of the film thickness on the number of ALD cycles was determined from X-ray fluorescence (XRF) measurements. In these studies, a TiO_2 film with a known thickness, measured by the X-ray reflection method with an accuracy of 1–2%, was used as a reference.

The sprayed TiO_2 films were obtained using a sol composed of TTIP (0.1 mol/l) and acetylacetone at molar ratio of 1:2 in ethanol. The sol was sprayed onto the substrate heated up to 450 °C employing 2–20 spray pulses consisting of 1 s spray and 30 s pause. The films obtained were amorphous according to Raman spectra. In more detail the films were characterized using X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM).

The solar cell structure was completed by chemical spray deposition of In_2S_3 buffer and $CuInS_2$ (CIS) absorber layers using precursor solutions of millimolar concentrations and deposition temperature close to 300 °C [8]. Thus, the solar cell structure could be presented as ITO/ZnO_{STR}/ZnO:In/TiO_2/In_2S_3/CIS. Planar solar cells (i.e. those without ZnO_{STR} layer) as reference samples were prepared simultaneously with the structured cells. The solar cells prepared were characterized by *I–V* curves in dark and under the halogen lamp illumination with intensity of 100 mW/cm^2. Surface morphology and cross-section views of the structures were examined by high resolution SEM on Zeiss HR FESEM Ultra 55 equipment.

3. Results and discussion

3.1. Effect of TiO_2 layer on chemical stability of ZnO nanorods

Manufacturing of solar cells based on ZnO nanorods has potential technological limitations. For instance, there is a basic requirement for the rods to be chemically stable. The use of chemical technologies such as chemical bath deposition or successive ionic layer adsorption and reaction (SILAR) to deposit the next component layers without protection of ZnO is questionable as ZnO is neither stable in acidic nor in alkaline solutions. SEM micrographs of ZnO nanocrystals before and after spraying an acidic solution (pH ~2.8) are presented in Fig. 1a. As can be seen, some of the crystals have been dissolved and those that remain have lost initially well developed hexagonal shape. Thus, it is extremely important to protect ZnO crystals from chemical dissolution when using chemical solution based techniques (solutions with high or low pH) to prepare the next component layers of the device. For this purpose a thin layer of a chemically inert material, which ideally would not degrade the electrical parameters of the device, could be applied onto the ZnO crystals. SEM micrograph of a ZnO nanorod array coated with a thin TiO_2 layer prepared by applying 50 ALD cycles (Fig. 1b) shows clearly that this layer exhibits sufficient chemical stability in chemical spray deposition process of the following CIS layer. According to XRF data (Fig. 2) the thickness of this TiO_2 layer did not exceed 1 nm.

3.2. Dependence of solar cell output parameters on the thickness of TiO_2 layer prepared by ALD

For the solar cells studied, the TiO_2 films were deposited using 50, 90 and 160 ALD cycles. In this way, the TiO_2 layer thickness was varied from 0.5–7 nm (Fig. 2). *I–V* curves of the structured cells with different TiO_2 thicknesses are presented in Fig. 3a. According to the *I–V* curves, the TiO_2 layer grown by applying 50 ALD cycles on structured cells resulted in an s-shaped *I–V* curve. A similar layer grown with 50 ALD cycles on a planar cell had, however, only weak influence on the output parameters. TiO_2 layers grown by applying 90 or more ALD cycles resulted in s-shaped *I–V* curves of both structured and planar cells. Nevertheless, the effect of the TiO_2 layer on the *I–V* curves was stronger in the case of structured cells than in the case of planar cells. The most probable reason for this dissimilarity is a difference in the nucleation of TiO_2 on ZnO with different surface structures. As can be seen in Fig. 2, practically no growth has been obtained during first 20–30 cycles on planar ZnO as well as on Si surface. XRF studies of the TiO_2 films grown on structured ZnO showed, however, somewhat faster nucleation. Unfortunately, because of complex surface morphology of the latter samples, estimation of the real TiO_2 thickness on these

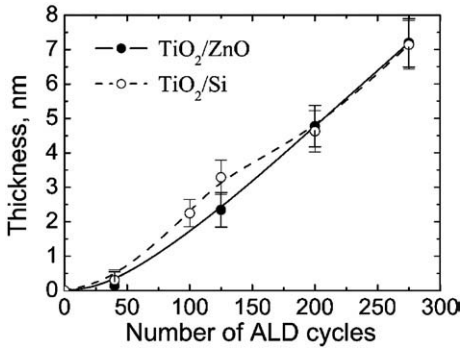

Fig. 2. Dependence of TiO_2 film thickness on number of ALD cycles.