Chapter

Doped Zinc Oxide Nanostructures for Photovoltaic Solar Cells Application

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Abstract

Zinc oxide and doping effects of Cu on its structural, morphological, optical, and surface wettability properties and the consequent influence on photoelectrochemical solar cell performance has been reviewed. Cu dopant in the doping solution is varied in the range of 1 to 5 at.% which significantly affected the properties of ZnO. Slight changes in the lattice parameters of the Cu-doped zinc oxide (CZO) electrodes were reported, due to the successful substitution of Zn^{2+} by Cu^{2+} and also enhancement in crystallinity of the films at 3 at.% Cu due to reduction in crystallographic defects in the film. Surface morphologies were reported with densely grown nanorods over the varied range of Cu, with 3 at.% having the densest microstructures with average diameter approximately 125 nm. A review of optical properties indicated significant enhancement in absorption edge of approximately 60 nm into the visible band for the nanorods with 3 at.% Cu content due to light scattering. Optical energy band-gaps decrease from 3.03 to 2.70 eV with Cu doping. Surface wettability was adjudged hydrophilic for all the films, implying high porosity and water contact angles depended on Cu content. Photoelectrochemical cell performance indicated an n-type photoactivity in sodium sulfate (Na_2SO_4) electrolyte, which motivates to check its feasibility in solar cell applications.

Keywords: zinc oxide, nanostructures, CZO, photoelectrochemical solar cells, Cu concentration, nanorods

1. Introduction

Zinc oxide is an inorganic compound having a chemical formula ZnO. It is a white powder which is nearly insoluble in water. It crystallizes in two main forms, the hexagonal wurtzite and cubic zinc blende. The wurtzite structure with lattice parameters $a = 0.3296$ and $c = 0.52065$ nm is found to be more stable than the zinc blende structure, and hence it is more widely used [1]. The ZnO structure is commonly described as consisting of a number of alternating planes composed of tetrahedrally coordinated O^{2-} and Zn^{2+} ions, stacked alternately along the c-axis without a central symmetry as illustrated in **Figure 1** [1, 2]. It is a group II–VI semiconductor with a wide band gap of about 3.33 eV. Due to its direct and wide band gap in the near-UV spectral region [3–5] and a large free exciton binding energy, it has become a promising functional semiconductor material, which possesses a wide range of novel applications. ZnO has been identified with many unique properties

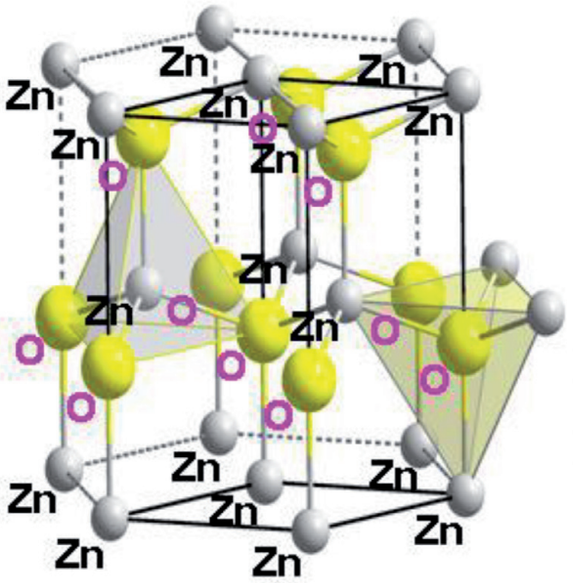

Figure 1.
Hexagonal Wurtzite crystal structure of ZnO [1].

such as excitonic emission at or even above room temperature, optical transparency in the visible range, high surface-to-volume ratio and quantum confinement effect [6], amongst others, which have motivated intensive study of the semiconductor during the last two decades. ZnO is mostly known to crystalize as an n-type semiconductor, whereas synthesis of the p-type is not generally easy [1, 7].

ZnO is simple to synthesize; both chemical and physical techniques are used to produce excellent epitaxial films. The most commonly used techniques to grow epitaxial films of ZnO include electrodeposition, spray pyrolysis, sol–gel process, successive ionic layer adsorption and reaction (SILAR), RF sputtering, chemical bath deposition (CBD), spin coating, electron beam epitaxy, laser evaporation and ion beam sputtering, amongst others [7, 8]. **Figure 2** illustrates the various synthetic techniques (chemical as well as physical) that are generally used to grow compound and alloys of ZnO. The choice of a particular technique would be guided by some factors such as the application intended for the synthesis, effectiveness of the technique and cost implication [10, 11]. ZnO has been identified as one of the semiconductors with the largest number of novel nanostructures such as nanocombs, nanorings, nanohelixes/nanosprings, nanobelts, nanowires, nanorods, nanotubes, nanocages, etc., with a wide range of technological applications [12–15]. Novel applications of ZnO nanostructures include optical modulator waveguide, photonic crystals, surface acoustic wave filters, varistors, photodetectors, gas sensors, light-emitting diode, photodiodes and solar cells, amongst others [12].

Photovoltaic (PV) application of ZnO nanostructures requires large internal surface area with porous and high surface roughness to support good penetration of electrolyte [13, 14]. Chemical techniques are very simple, much reliable and cost-effective for the synthesis of high-quality electrodes for PV application. Most especially, chemical bath deposition technique is very suitable for growing large area films of ZnO with fascinating properties for photoelectrochemical solar cells [15, 16]. This technique is suitable for growing ZnO nanostructures on many substrates including microscope glass and stainless steel [6].

In several applications such as optoelectronics, ZnO can be used as a complement or alternative to some semiconductors such as GaN, and many researches are ongoing globally to further improve the properties of the semiconductor [10]. Trying to control the unintentional n-type conductivity and to achieve p-type

that the porosity of the films increases upon thermal annealing at 673 K and with respect to increased concentration of Cu; thus, the water goes in to the pores and craves making contact angle hydrophilic [10, 28]. This means that the films would have large surface areas which for application such as DSSCs would mean better dye adsorption resulting to enhanced photo absorption. Also, lower values of contact angles are beneficial for electrolyte percolation through the porous film, which is very important for PEC solar cells. This result is in agreement with the earlier observations from XRD and SEM.

3.6 Photoelectrochemical (PEC) studies

Photoelectrochemical response of a solar cell is based on the junction between semiconductor and an electrolyte. The electrolyte plays an important role in PEC cell as a medium for charge transfer between the photoelectrode and counter electrode [10, 22].

The photoresponses of the CZO thin films were studied by forming typical configuration cells, n-CZO (stainless steel substrate)/0.1 M Na_2SO_4/platinum/SCE. These PEC cells are easy to form, and many processing steps of p–n junction have been simplified or eliminated. Since the junction with liquid is formed spontaneously upon contact, irregular-shaped single crystal or thin films can be used [10, 17]. The solution-based measurements allowed us to quickly test the quality of CZO film electrode as a solar cell material [10, 17].

Tyona et al. [10] reported the PEC performance of their CZO using current–voltage (I-V) characteristics of the annealed CZO thin films in the dark and under illumination with 80 mW/cm^2 as illustrated in **Figure 12a–c**. The anodic

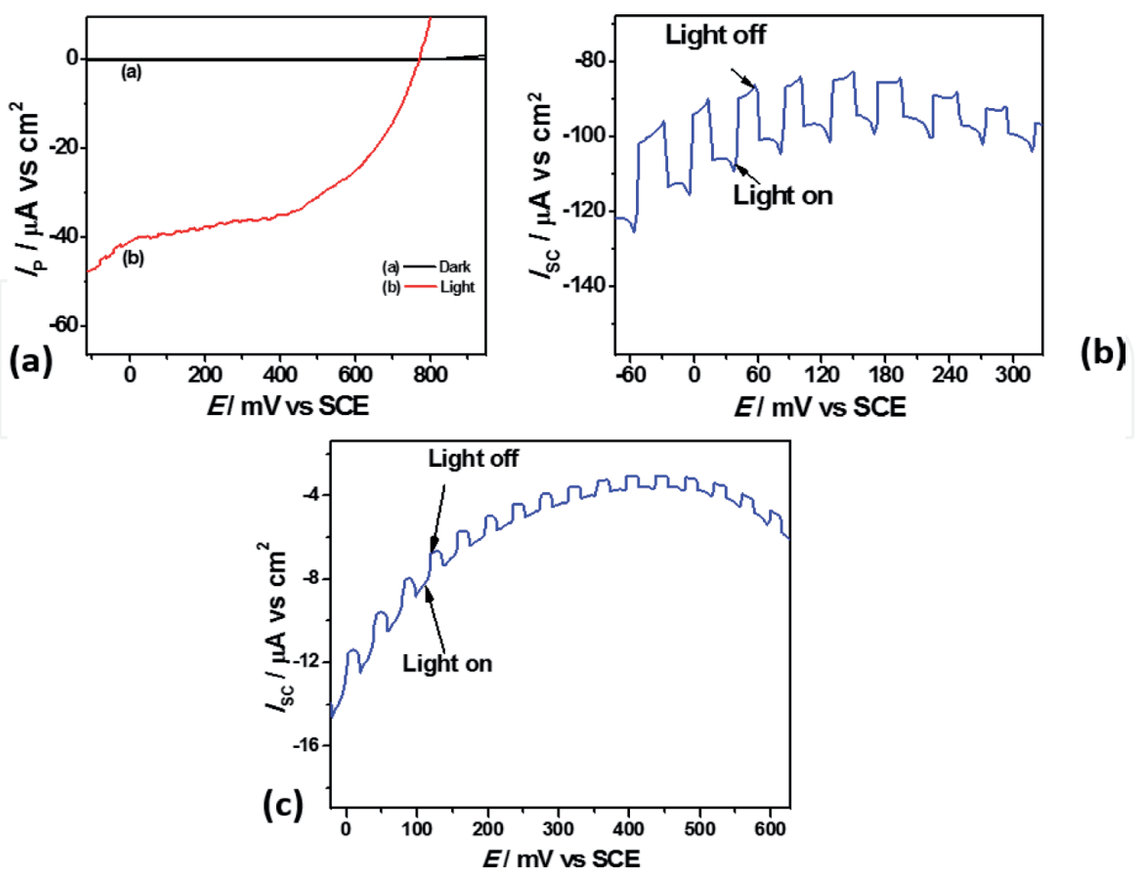

Figure 12.
Current-potential (I-V) curves of CZO thin films showing current and potential in the dark and under illumination for (a) 1%, (b) 3% and (c) 5% Cu concentrations [10].

ZnO electrodes	Photocurrent (I_{SC}) [μA/cm^2]	Photovoltage (V_{oc}) [mV]	I_{max} (μA/cm^2)	V_{max} (mV)	Efficiency η (%)	Fill factor (FF)
Undoped	12.34	388.0	9.00	230.0	0.0030	0.43
CZO (1%)	40.00	774.0	28.00	631.0	0.0220	0.57
CZO (3%)	98.00	796.0	74.00	667.0	0.0620	0.63
CZO (5%)	16.00	768.0	13.00	52.0	0.0009	0.06

Table 2.
Values of I-V measurement from PEC cells of CZO thin films [10].

photocurrent varied remarkably with the concentration of Cu in ZnO as reported with previous characterizations of the CZO. **Figure 12b** and **c** also represents the chopped light tests carried out in order to study the photosensitivity of CZO thin films. The photosensitivity confirmed that CZO absorber is an n-type material and is useful for the solar cell [10, 17]. The measured values of the PEC parameters with respect to Cu doping are shown in **Table 2**.

The photoelectrochemical measurement confirmed good photoactivities of the annealed CZO films prepared from simple CBD method. It is however observed that the photocurrent (short circuit current, I_{SC}) conversion efficiency and fill factor of the CZO film for 5% Cu are relatively low. This may be due to more compressive strain in the films at higher doping level as earlier explained in XRD which probably leads to a less dense nanostructure as illustrated in **Figure 7d** and consequently low photoactivity. The photocurrent obtained in the present study is not useful for most practical applications requiring high values of current; however, it is well known that conversion efficiency of such film can be considerably improved by thermal, chemical and photoelectrochemical surface treatments [10, 17].

4. Conclusions

This chapter examines ZnO and its numerous nanostructures and also considered doping as a measure for engineering the properties of ZnO for pre-determined applications. The chapter has also extensively reviewed the effect of Cu doping on structural, morphological and optical properties and surface wettability of chemical bath deposited ZnO thin films at various concentrations of Cu in the range 1–5% for PEC solar cell application. The review indicated that there were slight changes in the lattice parameters of the CZO electrodes which occurred due to the successful substitution of Zn^{2+} by Cu^{2+} and also enhancement in crystalline quality of the films at 3% Cu concentration due to the reduction in crystallographic defects in the film. A review of SEM studies showed densely grown nanorods over the varied range of Cu concentration, with the CZO nanorods of 3% having the most dense microstructures with average diameter approximately 125 nm. The density and diameter of the nanostructures demonstrated dependence on the amount of Cu dopant. A review of optical properties demonstrated that the incorporation of Cu dopant into ZnO introduced a shift in absorption edge of approximately 60 nm into the visible band for the CZO nanorods with 3% Cu content which is a significant enhancement in the optical properties of the films. Also, optical energy band gaps decrease from 3.03 to 2.70 eV upon Cu doping. Surface wettability was adjudged hydrophilic for all the films, which implied high porosity, and the size of water contact angles show dependence on Cu content. Photoelectrochemical cell performance indicated an n-type photoactivity in sodium sulphate (Na_2SO_4) electrolyte which motivate to check its feasibility in solar cell applications.

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Conflict of interest

I declare that there is no conflict of interest.

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