

Contents lists available at ScienceDirect

## Nano-Structures & Nano-Objects



journal homepage: www.elsevier.com/locate/nanoso

# Solution processed silver-nanowire/zinc oxide based transparent conductive electrode for efficient photovoltaic performance



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#### HIGHLIGHTS

#### GRAPHICAL ABSTRACT

- The Silver Nanowires (AgNWs) is demonstrated as transparent conductive electrode (TCE).
- The solution processed ZnO thin layer is deposited on AgNW film to TCE.
- The concentration of AgNWs as areal mass density of 242 mg/m<sup>2</sup> is found to be best as TCE.
- The enhancement in current collection of AgNW film is demonstrated using c-AFM.
- The CIGS solar cell exhibited efficiency of 13.5% using AgNW film as TCE.

#### ARTICLE INFO

Article history: Received 6 February 2018 Received in revised form 16 May 2018 Accepted 24 May 2018

Keywords: Energy storage and conversion Sol-gel preparation Deposition Solution process Transparent conductive electrode



#### ABSTRACT

To replace expensive and scarce Indium Tin Oxide (ITO) as transparent conductive electrode (TCE) in solar cell fabrication, low-cost and solution processed metal nanowires can also be used as a TCE due to its higher conductivity and transparency. Despite of its higher conductivity and transparency, bare Silver nanowire (AgNW) film suffers due to its poor adhesion and smaller contact area with lower-lying n-type buffer layer. In this work, percolation network of AgNWs covered with scalable and solution processed ZnO film as transparent conductive electrode (TCE) is demonstrated and utilized for fabrication of CuInGaSe<sub>2</sub> thin film solar cell. The concentration of the AgNWs in percolation network is optimized as areal mass density of AgNWs in the TCE. The conductive atomic force microscope studies are done to conclude the enhancement of current collection by covering the AgNW film with solution processed ZnO layer. The AgNW-based TCE with areal mass density of 242 mg/m<sup>2</sup>, sheet resistance 11  $\Omega$ /sq and transmittance 90% exhibited maximum conversion efficiency of 13.4% which is comparable to the efficiency obtained for vacuum based sputter deposited ITO or ZnO as TCE.

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#### 1. Introduction

Indium tin oxide (ITO) is commonly used as a conventional transparent conductive electrode (TCE) due to its high electrical conductivity and optical transparency [1–4]. However, due to

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https://doi.org/10.1016/j.nanoso.2018.05.009 2352-507X/© 2018 Elsevier B.V. All rights reserved. scarce indium, brittle nature of ITO film and expensive as well as slow deposition process, alternative materials are needed especially for flexible electronics [5,6]. To replace ITO, various materials have been prepared and applied as TCE for fabrication of different electronic devices including solar cells [7–15]. The alternative materials which have been used include oxide film [16], conducting polymer [17–19], graphene based TCE [20] and silver nanowire (AgNW) based composite films [21,22]. The AgNW-based TCE have attracted much attention due its high electrical conductivity and transparency [21,22] in solar cells. In addition to excellent conductivity and transparency, the AgNW ink can be deposited easily on the transparent and flexible substrate to fabricate TCE.

Although, AgNW films have excellent electrical and optical properties, it suffers due to weak adhesion with low-lying substrate, roughness of the film and thermal stability especially when applied as TCE in thin film solar cell fabrication [23,24]. Several research groups have made great efforts to minimize these drawbacks in TCE prepared using AgNWs [25-29]. The surface roughness and the adhesion can be improved by applying a thin layer of metal oxide films on the AgNW film. Such oxide films have been demonstrated to improve surface roughness by filling up the pores generated in AgNW percolation network as well as provide better adhesion by increasing contact area with low-lying surface [30]. The deposition of metal oxide film on the AgNW film is also believed to interconnect the AgNWs at the junction and increases the thermal stability of the AgNWs [20,21-31]. To elaborate, Yang et al. demonstrated that embedding random Ag-NWs networks in conductive ITO nanoparticles showed a sheet resistivity of 20  $\Omega$ /sq and an optical transmittance of 88.6% at 550 nm wavelength [30]. Using such composite electrodes as TCE, a solar cell efficiency (PCE) of 10.3% and 8.6% have been achieved for CuInSe<sub>2</sub> and Cu<sub>2</sub>ZnSn(S,Se)<sub>4</sub> solar cells [30,32] respectively. However, expensive indium have restricted the application on large. Kim et al. reported that embedding random AgNWs networks in direct current sputtered conductive ZnO layer exhibited a sheet resistivity of 8  $\Omega$ /sq and an optical transparency of 91% at 550 nm [33]. Cu(In,Ga) Se<sub>2</sub> solar cells using such TCE exhibited a PCE of 6.37%. This PCE was further improved to 11.03% by using sol gel spin-coating deposited AZO layers instead of direct-current sputtered ZnO layers. Han et al. demonstrated that embedding random AgNWs networks in pulsed laser deposited fluorine doped ZnO layer exhibited a sheet resistivity of 23  $\Omega$ /sq and an optical transparency of 90.4% at 550 nm [34]. However, afore-mentioned reports successfully demonstrated the use AgNWs percolation network as TCE but these methods involves the use expensive and toxic In metal or vacuum based deposition of In free TCE at temperature above 200 °C.

In our previous work, we have demonstrated the use of AgNWbased composite film covered with rf-sputtered deposited ZnO as TCE for fabrication of CuInGaSe<sub>2</sub> solar cell [21,31] and achieved the efficiency of about 13%. Although, the efficiency was high but ZnO was deposited by rf-sputtered vacuum based method. To fabricate fully solution processed TCE, both AgNW and ZnO film must be deposited using solution method to ensure large area and low-cost production.

In this paper, we demonstrated the completely solution processed method of deposition of AgNW covered with solution processed ZnO layer. The theoretical density of the AgNWs in the TCE as areal mass density (AMD) is determined and optimized for maximum transparency and conductivity which lead to the highest efficiency of the solar cell fabricated. The reason behind that is to develop only one process parameter as AMD to optimize the TCE deposited for maximum possible favorable optical and electrical properties. We fabricated the CuInGaSe<sub>2</sub> solar cell using AgNW film covered with solution processed ZnO as TCE having different AMD of AgNW and demonstrated the effect of theoretical density on the solar cell parameters.

#### 2. Experimental

All the chemicals used in the experiment were reagent grade from Sigma Aldrich. AgNWs were synthesized by the well-known polyol process as reported [21]. Briefly, PVP (M.W. 55000, 0.2 g) was mixed with 50 mL ethylene glycol, and the solution was



**Fig. 1.** ZnO covered AgNW film deposited by one time (S0), two times (S1), three times (S2) and four times (S3) spin coating of the AgNW ink (scale bar is  $1 \mu m$ ).

stirred at room temperature for complete dissolution of PVP. After complete dissolution of PVP, 0.50 g of AgNO<sub>3</sub> was added under stirring to dissolve AgNO<sub>3</sub>. After dissolving AgNO<sub>3</sub>, 3.5 g of FeCl<sub>3</sub> solution (600  $\mu$ M) was added as metal assistance for growth of AgNW. Finally, the solution was transferred in preheated reactor at 130 °C and the reaction was continued for 3 h. The obtained Silver color product was washed using acetone and ethanol and centrifuged at least three times to collect the pure AgNWs free from PVP. Finally, the AgNWs were dispersed in ethanol to prepare 2 wt% AgNW ink. The AgNW film was deposited by spin-coating AgNW ink at 1000 rpm for 10 s and drying at 70 °C after each coating. The samples were designated as S0, S1 S2 and S3 for one time, two times, three times and four times spin coating of the AgNW ink in ethanol. To deposit the ZnO film, precursor solution of Zinc acetate was prepared by dissolving zinc acetate  $[Zn(CH_3COO)_2 \cdot 2H_2O]$ were dissolved in 2-methoxyethanol (CH<sub>3</sub>OCH<sub>2</sub>CH<sub>2</sub>OH) and monoethanolamine (NH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH). Equimolar amounts of zinc acetate and monoethanolamine were used. After being stirred for 2-3 h, the solution was aged for 48 h. The transparent solution obtained after aging for 48 h is the ZnO precursor solution. The ZnO layer was deposited on spin-coated AgNW film using spin coating at 2000 rpm for 30 s and dried at 150 °C. The TCE deposited on the glass was characterized by using FE-SEM with EDAX (JEOL-JSM at accelerating voltage of 300 kV) and X-ray diffraction (Rigaku Rapid Rint XRD) for morphological measurement and UV-Visible (UV-Vis) spectrometer (Lambda 40, Perkin Elmer) for transmittance measurement. Conductive AFM (C-AFM) (Nanoscope, Bruker) was used to characterize current extraction nature of TCE under 0.1 V of bias voltage in contact mode.

For fabrication of solar cell, co-evaporated CIGS film was used as absorber layer [21]. The current density–voltage (J–V) curve of the CIGS solar cell was measured by using source meter (Keithley 2400) under AM 1.5G filtered illumination of 1000 W m<sup>-2</sup> Xe lamp (Abet Technology), which was calibrated with Si reference cell.

#### 3. Result and discussion

The morphology of the solution processed ZnO coated AgNW was studied using FESEM as shown in Fig. 1. The diameter and length of the AgNW synthesized was found to be approximately 60

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