Solar Energy Materials and Solar Cells 174 (2018) 584–592

Contents lists available at ScienceDirect

Solar Energy Materials and Solar Cells

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

Solution-processed composite electrodes composed of silver nanowires and aluminum-doped zinc oxide nanoparticles for thin-film solar cells applications

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ARTICLE INFO

Keywords:
Silver nanowires
Aluminum-doped zinc oxide nanoparticles
Composite electrode
Solar cell

ABSTRACT

Transparent conducting electrodes based on silver nanowires (AgNWs) have arisen great interest due to their excellent photoelectric properties compared with the conventional sputtered indium tin oxide (ITO) electrodes. However, the practical applications of these electrodes are limited due to their coarse surface morphology, weak mechanical adhesion and high junction resistivity as well as poor thermal and chemical stability. In this work, we develop a new processing technique to resolve all above limitations by embedding random AgNWs networks in solution-processed conductive aluminum-doped zinc oxide nanoparticles (AZO-NPs) matrices via a spin-coating process at low temperature (150 °C). Our results show that coating the AZO-NPs on the surface of AgNWs networks effectively fill the holes between AgNWs and tightened the AgNWs junctions, resulting in ultralow surface roughness and excellent wire-substrate mechanical adhesion. Surrounding the AgNWs by conductive AZO-NPs could provide more electron transport channels between AgNWs so as to improve the wire-wire electrical conductivity. The resulting composite electrodes demonstrated an excellent performance with low sheet resistivity < 28 Ω/sq, high optical transmittance > 91% at 550 nm, excellent thermal stability at temperature as high as 270 °C, good chemical corrosion resistance, and retained high electrical conductivity showing less 1% deviation in sheet resistivity after 300 continuous convex and concave bending cycle. Kesterite pure sulfide Cu_2ZnSnS_4 thin film solar cells using such composite electrodes as top contact show a best conversion efficiency of 7.45%, achieving a 11.5% increase compared with conventionally sputtered ITO-based CZTS thin film solar cells due to higher short circuit current density and fill factor.

1. Introduction

Transparent conducting electrodes with high transparency and high conductivity are key components in optoelectronic devices such as touch screens, thin film solar cells, liquid crystal displays, and light-emitting diodes [1–3]. Currently, indium tin oxide (ITO) is the most commonly used transparent electrode materials in the above applications because of its excellent conductivity and transparency (10–20 Ω/sq at 85–90% transmittance) [4,5]. However, with the increased demands for electrode materials that are flexible, low-cost and capable of large-scale fabrication, current ITO electrodes suffer from the scarcity of high-cost indium and its brittle nature [6,7]. In this regard, nanomaterials such as carbon nanotubes (CNTs) [8,9], graphene [10], metal grids or metal nanowires (NW) [11–13], and hybrids of these [14,15], have been actively studied as promising substitutions. Among these candidates, metal nanowires are more promising due to its higher conductivity of metal in comparison with those of the carbon-based CNTs and graphene [16,17]. In addition, metal nanowires show many merits, such as solution-processability, low-cost fabrication, potential high-throughput and flexibility [18]. Lee et al. first demonstrated silver nanowire (AgNWs) transparent conducting electrode on glass substrate using the solution dispersed AgNWs via a simple spin-coating process [19]. Currently, various reports have demonstrated that AgNWs electrodes exhibit conductivity less than 20 Ω sq^{-1} and transparency higher than 90% at 550 nm [20–24], which potentially replace ITO electrodes in the current electronic industry. However, the practical applications of AgNWs electrodes in optoelectronic devices are limited because of their coarse surface morphology, weak mechanical adhesion, loose

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http://dx.doi.org/10.1016/j.solmat.2017.09.042
Received 22 March 2017; Received in revised form 22 September 2017; Accepted 22 September 2017
Available online 12 October 2017

contact between AgNWs, high junction resistivity and poor thermal and chemical stability [25]. More importantly, there are many void regions between AgNWs resulting in conductivity inhomogenity and incomplete electrical contact to the active area of the device, which may lower electron transport and carrier collection efficiency especially for photovoltaic cells [26]. Many processing methods have been reported to address these issues, including thermal annealing [27], mechanical pressing [28], nanoscale joule heating [18] plasmonic welding [29], and layers transfer [30], et al. Unfortunately, these methods either require high input powers or high temperature sintering [28] or suffer from obvious scalability issues and complex fabrication steps [31]. Therefore, there is an urgent need to develop a new processing method and materials structures to overcome all afore mentioned problems of AgNWs electrodes.

It is reported recently that embedding random AgNWs networks in conductive metal oxides can resolve all above issues regarding the AgNWs electrodes for photovoltaic cells applications [3,32–36]. The introduced conductive metal oxides are considered not only to fill the void regions between AgNWs for a smooth morphology, but also to protect the AgNWs from oxidation/corrosion when they are directly exposed to air. Moreover, AgNWs surrounded by conductive metal oxides can improve wire–wire conductivity. For instance, Yang et al. reported that embedding random AgNWs networks in conductive ITO nanoparticles showed a sheet resistivity of 20 Ω/sq and an optical transmittance of 88.6% at 550 nm wavelength [32]. Using such composite electrodes as top contact, a power conversion efficiency (PCE) of 10.3% and 8.6% have been achieved for $CuInSe_2$ solar cells [33] and $Cu_2ZnSn(S,Se)_4$ solar cells [34], respectively. However, high cost of indium must be taken into account for large scale applications. Kim et al. reported that embedding random AgNWs networks in direct current sputtered conductive ZnO layer exhibited a sheet resistivity of 8 Ω/sq and an optical transparency of 91% at 550 nm [35]. $Cu(In,Ga)Se_2$ solar cells using such composite electrodes as top contact offered 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 [3]. Han et al. reported that embedding random AgNWs networks in pulsed laser deposited fluorine doped ZnO (FZO) layer exhibited a sheet resistivity of 23 Ω/sq and an optical transparency of 90.4% at 550 nm [36]. Perovskite solar cells using such composite electrodes as front electrodes offered a PCE of 3.29% [36]. Though the direct current sputtered ZnO layer and pulsed laser deposited FTO layer were indium-free, the use of the vacuum equipments made them less cost-effective. Furthermore, the preparation of the sol-gel deposited AZO layer requires an annealing temperature up to 200 °C, which might be not suitable for fabricating devices on the flexible substrates such as polyethylene terephthalate (PET) and polycarbonate (PC) with the glass transition temperature in the range of 75 − 147 °C [37].

In this work, in an attempt to resolve all these afore mentioned problems of the AgNWs electrodes, we developed a new processing method by embedding random AgNWs networks in solution-processed conductive aluminum-doped zinc oxide nanoparticles (AZO-NPs) matrix, which was fabricated by sequentially stacking AgNWs networks and AZO-NPs through a spin-coating process at temperature as low as 150 °C. The fabrication process is simple and easily achieved, as it avoids using expensive vacuum equipments and sintering at high temperature. More importantly, the use of high cost indium element is avoided. We thoroughly investigated the microstructural, optoelectronic and mechanical properties as well as thermal and chemical stabilities of the composite electrodes. The resulting composite electrodes exhibit an excellent performance with low surface roughness, high conductivity of < 28 Ω/sq, high optical transmittance of $> 91\%$ at 550 nm, excellent mechanical adhesion and flexibility, good thermal stability at temperature as high as 270 °C and excellent chemical corrosion resistance. To demonstrate the potential applications of the composite electrodes, we also employed them in kesterite pure sulfide Cu_2ZnSnS_4 thin film solar cells that showed a PCE of 7.45%.

2. Experimental section

2.1. Materials

Ethylene glycol, ethanol, poly vinylpyrrolidone (PVP), silver nitrate ($AgNO_3$), silver chloride (AgCl), potassium bromide (KBr) and polyvinyl alcohol (PVA) were purchased from Sigma Aldrich and used without further purification unless stated otherwise. Super white glass substrate of 2 mm thickness and polyethylene terephthalate (PET) substrate of 0.2 mm thickness were purchased from available commercial sources. Before using, all of the substrates were treated by ultrasonic cleaning in detergent, acetone, isopropanol, deionized water and ethanol for 15 min, followed by drying in air and storing in a vacuum drying box. The AZO-NPs dispersed in isopropanol with mean grain sizes of 20 nm was purchased from available commercial sources.

2.2. Synthesis of AgNWs solution

The AgNWs was synthesized by using a polyol method [20]. In a typical procedure, 1.336 g of PVP and 0.020 g of KBr was added into 40 mL of ethylene glycol in a flask, followed by heating up to 170 °C. Once the temperature was stabilized, 0.100 g of AgCl was added into the flask for initial nucleation of the silver seeds. After five minutes, a solution of $AgNO_3$ (0.44 g dissolved in 4 mL of ethylene glycol) was injected into the flask over 10 min. Then, the solution was heated at 170 °C for additional 30 min and allowed to cool down at room temperature for several hours, forming a light brown suspension. The precipitate was collected and sequentially dispersed into 50 mL of methanol and centrifuged several times at 4000 rpm for 30 min to remove solvent (ethylene glycol), PVP, and other impurities. The collected silver nanowires were finally dispersed in ethanol according to the desired concentration.

2.3. Fabrication of composite electrodes and CZTS thin film solar cell

The composite electrode was fabricated by sequentially stacking AgNWs films and AZO-NPs layer via a simple spin-coating method. The concentration of AgNWs solution used for deposition of AgNWs films was 2.5 mg/mL. The AZO-NPs dispersion was prepared by mixing equal volumes of 10 wt% of AZO-NPs dispersed in isopropyl alcohol and 0.1 wt% of zonyl surfactant dissolved in deionized water. The added zonyl surfactant was used to improve the wettability of the AZO-NPs dispersion. In order to improve the mechanical adhesion of the resulting AgNWs/ITO-NP composite electrode, 1.0 wt% polyvinyl alcohol (PVA) was also added to the AZO-NPs dispersion according to a previous report [32]. The AgNWs films were deposited on a glass or a PET substrate with varied rotating speeds from 2000 rpm to 5000 rpm for 30 s, followed by drying at 120 °C for 30 s on a hot plate in air. UV radiation exposure of the deposited AgNWs films was performed using a 250 W UV-handheld apparatus (5 cm distance to substrate and spectrum range from 185 nm to 254 nm) with an iron doped Hg lamp. The AZO-NPs layer was then deposited at the surface of the AgNWs films with rotating speed at 3000 rpm for 30 s, followed by drying at 120 °C for 60 s. After that, the composite electrodes were annealed at 150 °C in air for additional 10 min Fig. 1 showed the schematic diagram used for the deposition of composite electrodes. The CZTS thin film solar cells were fabricated according to our previous report [38]. The process was achieved by means of DC sputtering 1000-nm-thick Mo layer as back contact on glass substrate, spin-coating deposition of 1000-nm-thick CZTS layer as absorber, chemical bath deposition of 70-nm-thick CdS layer as buffer layer, and spin-coating deposition of 250-nm-thickness composite electrodes as top contact to replace the sputtered-deposited ITO electrodes. The effective active area of the completed device was 0.45 cm^2.