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ORIGINAL PAPER

Efficient, low-dimensional nanocomposite bilayer CuO/ZnO solar cell at various annealing temperatures

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Abstract
In this work, heterojunction, solar cells based on inorganic semiconductors were fabricated at various thermal-annealing temperatures using vapor deposition techniques. The active layer primarily consists of a bilayer comprising a hole transporting copper oxide-CuO and an electron transporting zinc oxide-ZnO nanoparticles. It was observed that the power conversion efficiency-PCE increased from 0.06 to 0.08% with an increase in annealing temperature from 400 to 500 °C, possibly, as a result of increased absorption, in the visible region with increasing temperature. A significant increase in the crystallinity of single and bilayer films was also observed with increasing annealing temperature.

Keywords Inorganic semiconductor · ITO · CuO · ZnO · Bilayer · PCE

Introduction

Among the renewable energy resources, photovoltaic can be an increasingly appealing option to meet world's energy requirements [1]. Photovoltaic conversion of solar energy into electricity represents a clean and abundant energy source. To pave the path towards efficient and affordable photovoltaics, an extensive research work is in progress. High-purity expensive material-based silicon solar cells achieved the efficiency up to 24% [2]. However, Si-based solar cells are not convenient because of excessive fabrication costs, requirements of large surface area and their limited functionality in the absence of sunlight. Thin film-based organic photovoltaics (OPVs) can potentially be alternative to Si-based solar cells because of being cost-effective, lightweight and easy to process [3]. But, organic photovoltaics demonstrate poor efficiency and are not chemically stable over long periods of times.

This instability can be avoided using inorganic semiconductors CuO, Cu_2O, TiO_2, NiO and ZnO, that have a wide range of remarkable electrical and optical properties, for solar cells [4–9]. A small number of p-type metal oxide semiconductors exist, providentially CuO is a prominent semiconductor (SC) with a band gap—B.G of 1.5 eV which is matching with the ideal B.G (1.4 eV) required for a solar cell. It also has high optical absorption, is relatively non-toxic and an abundant raw material [10]. Another suitable material can be ZnO which works as an n-type SC, has a B.G of 3.37 eV, absorbs UV light while being highly transparent to the visible region of the solar spectrum [11]. Despite its wide range of applications, a few reports have been published about CuO-based photovoltaic devices. Lim et al. reported 0.04% efficiency for devices based on CuO and phenyl-C61-butyric acid methyl ester (PCBM) [12], while CuO-C_{60} core–shell junction cells were reported with a PCE of 0.02% [13]. Gao et al. reported a p-CuO/n-Si device has 1% PCE [14]. Sputter deposited AZnO/ZnO/CuO/NiO heterojunction architecture attained efficiency up to 0.08% for 500-nm-thick CuO films [15]. Low-dimensional CuO structures (nanorods and nanofibers) are being used in hybrid and DSSC-dye-sensitized solar cells [16, 17]. Recently, our group reported CuO nanoparticles (≤ 50 nm) employed in the polymer-active layer using inverted architecture to increase light absorption range, thereby improving the PCE of devices doped with CuO nanoparticles [18]. Furthermore, ZnO nanoparticles (≤ 100 nm) had been added in the (P3HT + PCBM) active layer of the hybrid organic solar cell to increase the electron mobility in the active layer leading

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to a remarkable increase in PCE as compared to devices without nanoparticles [19]. A heterojunction device based on ZnO nanowires coated by CuO has been reported with a PCE up to 0.3% [20]. Omayio et al. reported maximum PCE 0.232% for Sn-doped ZnO/CuO solar cell [21]. In the literature, the maximum reported PCE reported for CuO/ZnO nanocomposites-based device is 1.1×10^{-4} [22]. However, CuO-based photovoltaics are predicted to demonstrate theoretical power conversion efficiency up to 30% by considering only radiative recombination [23].

In an attempt to achieve higher efficiency in inorganic nanocomposite solar cells, we fabricated CuO/ZnO ($\leq$ 50 nm) heterojunction devices using vapor deposition techniques at various annealing temperatures. The low-dimensional bilayer structure of nanoparticles compared with the bulk materials exhibit large surface area for efficient light absorption and shortened collection length for charge carriers responsible for increasing power conversion efficiency [24]. The carrier lifetime and diffusion length for CuO are approximately 460 ps and 40 nm, respectively. Low-dimensional structures could provide better carrier collection due to reduced collection length of charge carriers [15, 25]. The fabricated devices were fully characterized using various techniques.

Experimental details

Materials

CuO and ZnO nanoparticles ($\leq$ 50 nm) were obtained from Sigma-Aldrich. Indium-doped tin oxide-ITO-coated glass slides of sheet resistance, R_{sh} (20–25 Ω/sq) were acquired from Lumtec, Taiwan.

Device fabrication

ITO glass slides were cleaned using soap, distilled water, IPA and ethanol each for 15 min in an ultrasonic bath. First, CuO films with thickness 200 nm were deposited on cleaned ITO using high resistive and voltage thermal evaporator (Leybold-Heraeus, A-550 V) under high vacuum at a constant evaporation rate of (0.5 Å/S). The deposited films were annealed at 400 and 500 °C for 1 h, respectively. Upon annealed films, ZnO films of 100 nm thickness were deposited by an electron beam evaporator (E-Beam) (Leybold-Heraeus, A-550 V) and annealed at 400 and 500 °C in the air. Finally, top contacts of aluminum (Al) 100-nm-thick were deposited by the thermal evaporator. Resulting device structure (ITO/CuO/ZnO/Al) is shown in Fig. 1. The calculated device area was 0.0765 cm^2.

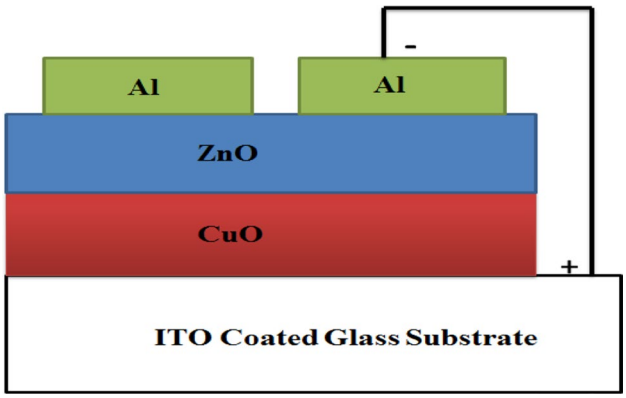

Fig. 1 Schematic representation of the bilayer-structured device

Characterization

The *J–V* characteristics were recorded by Keithley source meter (2420) connected with a (CT 100 AAA) solar simulator under standard condition (AM 1.5 G, 100 mW/cm^2). Genesys 10S (UV–Visible) spectrophotometer was used for optical properties of deposited films. The morphological and structural analysis of deposited films were carried out by SEM (JSM-6480LV JEOL) operating at 20 kV and (PAN Analytical, Ltd), respectively.

Results and discussion

Figure 2a, b shows X-ray diffraction-XRD spectra of single- and bilayer-deposited films at various annealing temperatures. Subsequent analysis confirmed the growth of ZnO hexagonal wurtzite phase that was indexed to JCPDS 01-089-0510 (2c) and improvement in the crystal quality through heat treatment. The XRD spectrum of CuO was indexed to JCPDS 01-080-1917 (2c) confirmed the growth of pure CuO monoclinic phase and an increase in the crystallinity at higher temperatures. The XRD spectrum of bilayer device yields the intense peaks arising from both CuO and ZnO respective phases. The peak around 31° was corresponding to ITO substrate confirmed by JCPDS 00-032-0458 (2c). The crystallinity of bilayer film was improved with increasing annealing temperature.

The measured absorption spectra of deposited films are shown in Fig. 3a, b. An increase in absorption in the visible region was observed for CuO at 500 °C. This increase in absorption can be attributed to the growth of highly crystalline and densely packed nanoparticles as it is evident from XRD and SEM results discussed later. The absorption spectrum of bilayer structure shows absorption peaks in both UV and visible region confirming the presence of CuO

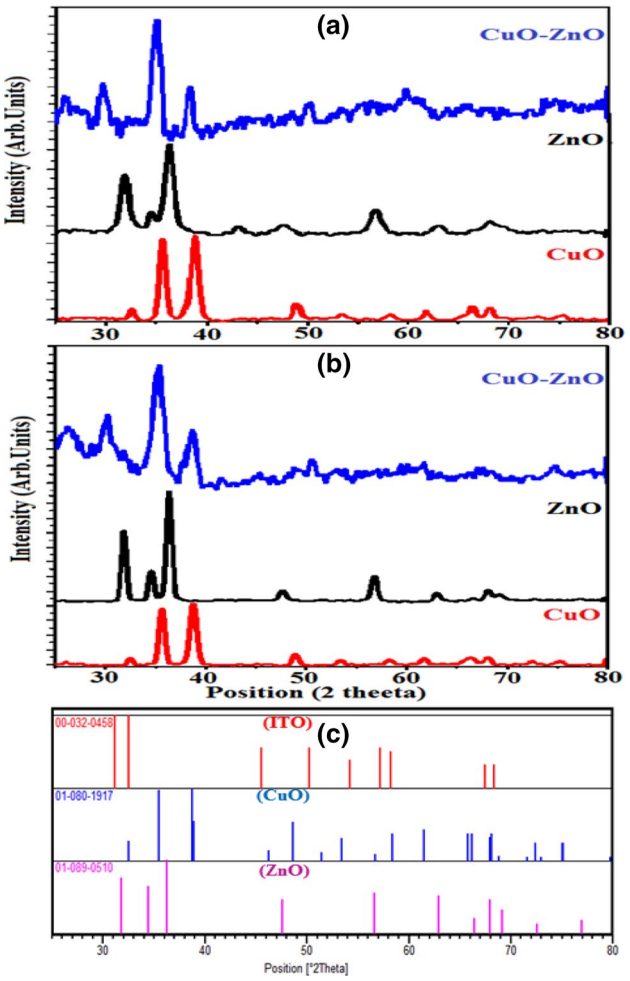

Fig. 2 X-ray diffraction pattern of single and bilayer films at 400 °C (**a**) at 500 °C (**b**) reference patterns (**c**)

and ZnO in the bilayer device. The absorption spectrum of bilayer also indicates a considerable increase in the absorption window when compared with CuO and ZnO individual spectrum.

Transmittance spectra of deposited films is presented in Fig. 4a, b. It can be clearly seen that ZnO film is highly transparent to visible region relative to CuO and this transmission is not affected by scattering of light from densely packed nanoparticles in low-dimension structure.

The band gap for CuO, ZnO and bilayer structure is calculated to be 1.61, 3.23 and 1.70 eV, respectively (Fig. 5).

Figure 6a–f display the FESEM images of single and bilayer nanocomposite films annealed at different temperatures. The images of ZnO, CuO and bilayer films annealed at 400 °C revealed a sort of rough surface of a continuous integrated network of nanoparticles (Fig. 6a–c). With increasing annealing temperature, densely packed round-shaped nanosized particles ($\leq$ 50 nm) of uniform shape and size were found on the surface (Fig. 6d–f). The top view of the bilayer (device), prior to Al contact deposition (Fig. 6c, f) represent a smooth surface at high annealing temperatures, apart from few small and large grains which are mostly looking like dust-particles. The deposited films are free of pinholes and cracks. These images confirm the growth of densely packed nanoparticles.

The proposed energy level diagram to fabricate a device is shown in Fig. 7 [18, 19]. Excitons (electron–hole pairs) are produced at the CuO and ZnO interface. The conduction band—C.B energy offset between metal oxides secures that "es$^-$" can be transferred to the n-type ZnO easily and move toward the respective electrode, Al and holes transfer toward ITO electrode.

Figure 8 represents the *J*–*V* curves of prepared hybrid devices attained under dark and 1-sun conditions of (100

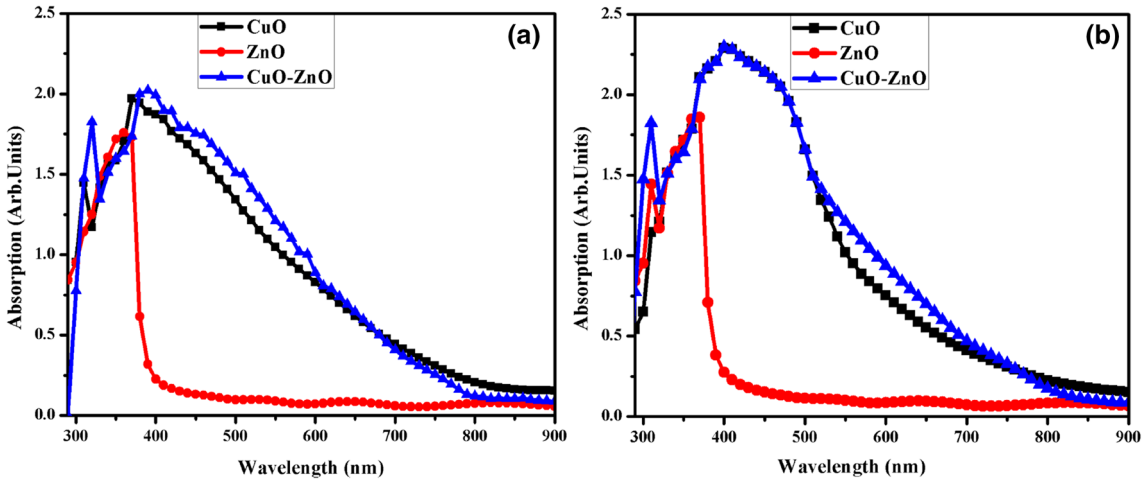

Fig. 3 UV–Vis absorption of distinct and bilayer films at 400 °C (**a**) and at 500 °C (**b**)

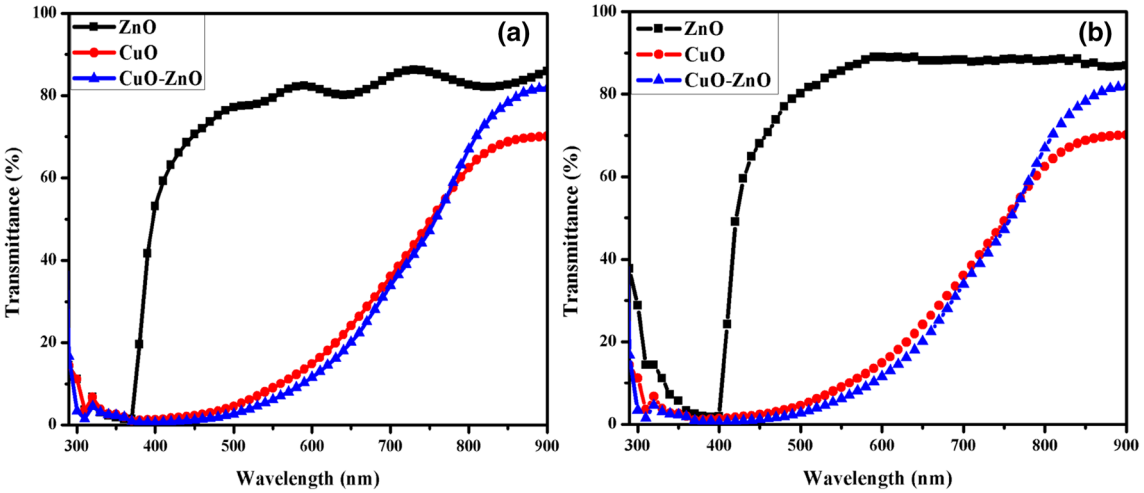

Fig. 4 Transmittance spectra of single and bilayer films at 400 °C (**a**) at 500 °C (**b**)

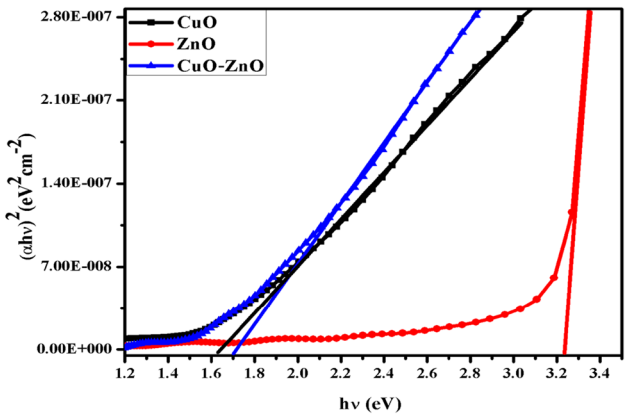

Fig. 5 Tauc plots for single and bilayer films at 500 °C

mW cm^{-2}). In dark, both devices show diode behavior and graph shifts down under illumination as solar cells start generating power. The electrical parameters for the devices annealed at 400 and 500 °C extracted from *J*–*V* curves (in Fig. 8a, b) are summarized in Table 1. A significant increase in electrical parameters, namely FF-fill factor, J_{sc}-short-circuit current density and PCE was observed with increasing temperature. The device performance is high at higher temperature due to the better crystal and interface quality as described in a previous study as well [26]. The best-achieved PCE is 0.08% which is primarily due to low J_{sc} and V_{oc}. The obtained PCE is higher relative to previously reported one for CuO/ZnO thin film heterojunction solar cells [22]. The PCE of CuO/ZnO heterojunction device is compromised through the short carrier's diffusion length, poor life time

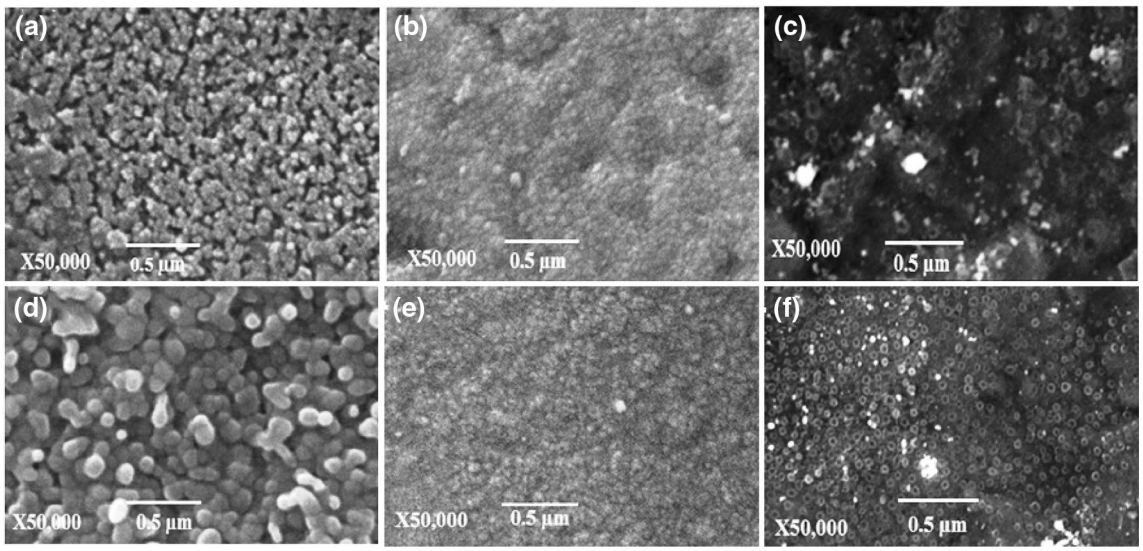

Fig. 6 SEM images of ZnO (**a**) CuO (**b**) and bilayer films (**c**) at 400 °C and (**d–f**) at 500 °C, respectively

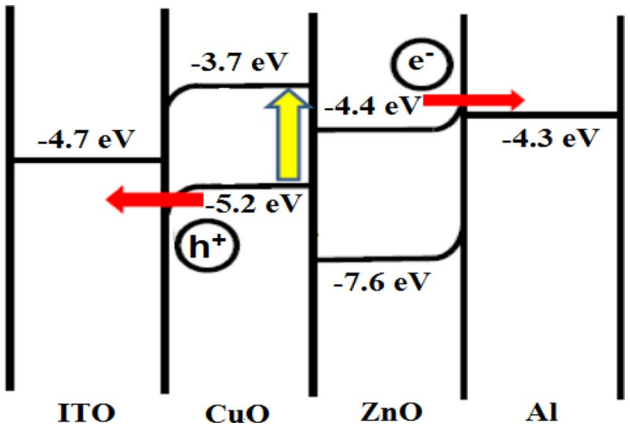

Fig. 7 Energy level diagram of ITO/CuO/ZnO/Al device

in CuO and carrier recombination at CuO/ZnO interface. Despite this, CuO is still a hopeful material for thin absorber layer devices. It can increase the absorption of the active region leading to an increased J_{sc} [27–29]. Although PCE reported in the present work is low, however, using low-dimensional nanoparticle-based active layer, the J_{sc} and V_{oc} can be improved due to efficient charge separation and collection at the interface because of reduced collection length of photogenerated charge carriers.

Table 1 Solar cell parameters at different annealing temperature

Device parameters	400 °C	500 °C
J_{sc} (mA/cm^2)	0.44	0.55
V_{oc} (V)	0.26	0.26
FF (%)	0.60	0.62
PCE (%)	0.06	0.08

Conclusion

Inorganic semiconductor-based solar cells were fabricated using a low-dimensional bilayer structure of CuO and ZnO ($\leq$ 50 nm) nanoparticles at various annealing temperatures. The XRD analysis showed improvement in the crystallinity of deposited single and bilayer films through annealing temperature. SEM images display smooth surface of deposited layers with densely packed nanoparticles of uniform size and shape at 500 °C. An increase in the absorption for CuO in the visible region and for ZnO in UV region was observed which leads to enhancing J_{sc} of the device and ZnO is highly transparent in the visible region for solar spectrum. The PCE of the devices increased from 0.06 to 0.08% with increasing temperature from 400 to 500 °C, respectively. The improved device performance at higher temperature is attributed to better crystal and interface quality. Both the

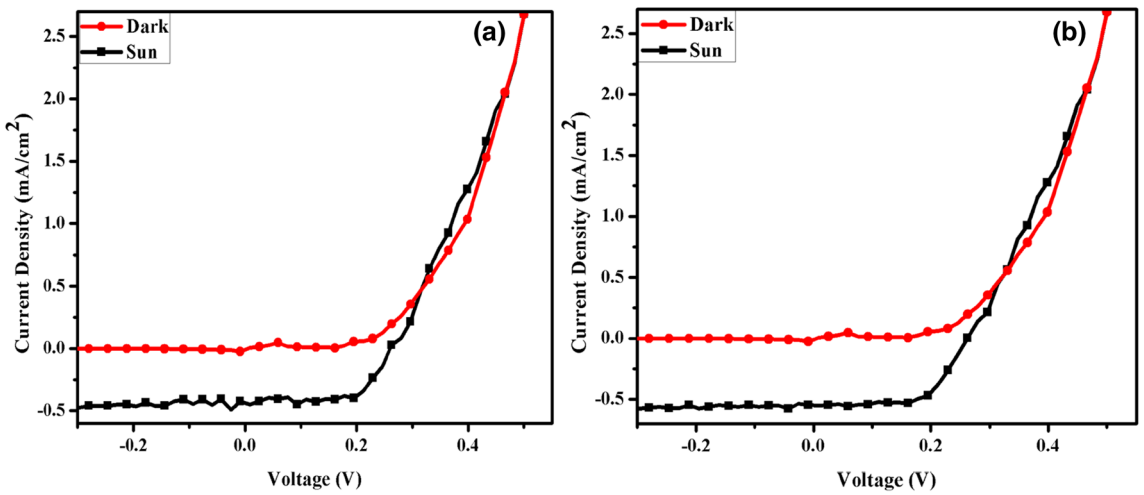

Fig. 8 *J–V* characteristics curve of device fabricated at 400 °C (**a**) at 500 °C (**b**)

CuO and ZnO can be used in the polymer-active layer to increase the absorption as well as collection of electrons. In this way, high-efficient quaternary blend hybrid organic solar cells can be achieved with good stability.

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