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Fabrication of transparent ZnO/(CuZn)O heterojunction solar cells by electrochemical deposition

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Abstract

Transparent (CuZn)O thin films were fabricated via electrochemical deposition at room temperature from an aqueous solution containing Zn(NO₃)₂ and Cu(NO₃)₂, and properties of the films were studied before and after annealing at 400 °C in air. According to x-ray photoelectron spectroscopy results, copper was in the Cu⁺ oxidation state. All the samples before and after the annealing were found to be amorphous by x-ray diffraction, and p-type conductivity was found by photoelectrochemical characterizations. Transparent p-n heterojunction ZnO/(CuZn)O was fabricated by depositing ZnO on as-deposited and annealed (CuZn)O. For both as-deposited and annealed (CuZn)O, rectifying characteristics and photovoltaic effects were observed.

1. Introduction

Transparent solar cells (TSC) have attracted considerable attention since TSC is applicable to glass panels used in our daily lives, such as building and car windows [1]. This invention has a high potential of turning every glass surface in the advanced world into a solar panel [2]. However, there is one major obstacle for realizing this technology, that is, synthesis of good p-type transparent materials.

Zinc oxide (ZnO) is one of popular transparent conducting oxides (TCOs). It is an inexpensive and environmentally friendly material with high transparency in visible region in its thin film form [3, 4]. It is widely used in many important applications, as an n-type semiconductor in solar cells, photodetectors, sensors, transistors, light emitting diodes (LEDs), and also as a conductive layer (electrode) in various optoelectronic devices. ZnO is feasible owing to its good electrical, optical and piezoelectric properties [5–10]. It has an n-type conductivity with wide bandgap around 3.35 eV and resistivity as low as 10⁻³ Ωcm with proper doping [11, 12]. In contrast to n-type ZnO, fabrication of p-type ZnO films can be difficult due to the self-compensation effects by intrinsic defects and large ionization energy of acceptors [13].

Cu-doped ZnO or (CuZn)O alloy has attracted considerable attention as a potential material used for developing a wide range of advanced applications including LEDs, field effect transistors, catalyst, field emission arrays, energy storage, and solar cells [14–18]. Deposition of p-type (CuZn)O has been reported by various techniques previously such as hydrothermal synthesis [19], atomic layer deposition [20], sputtering [21, 22], spray deposition [10, 23], and electrochemical deposition (ECD) [24, 25].

Among these methods, ECD is one of the most useful approaches to prepare semiconductor thin films due to good controllability of growth rate through the control of various deposition parameters. Moreover it is capable of deposition on complex shapes and of large-scale production, with economical and environmental-friendly processing [25–27]. ECD of ZnO usually proceeds at high temperatures (60 °C–90 °C) [24, 28], and amorphous ZnO and/or Zn(OH)₂ is formed by decreasing the deposition temperature [29]. In our previous work, p-type amorphous (CuZn)O was successfully deposited at room temperature (RT) by ECD [25].

In this study, firstly, p-type (CuZn)O is deposited by potentiostatic ECD on indium tin oxide (ITO)-coated glass substrates under different condition. Then those films are annealed in 400 °C air, and electrical and optical properties are investigated. Secondly, n-type ZnO is deposited on both as-deposited and annealed (CuZn)O by
Figure 1. AES spectra for the as-deposited and 400 °C-annealed (CuZn)O samples fabricated with 1 mM Cu(NO₃)₂ and different Zn (NO₃)₂ concentrations.

Figure 2. Cu/Zn composition ratio for the as-deposited and annealed samples as a function of Zn(NO₃)₂ concentration in the solution.
galvanostatic ECD to fabricate ZnO/(CuZn)O hetrojunctions. The heterojunction samples exhibit high optical transmission, i.e., around 65% in the visible region, and rectifying properties and photovoltaic effects are confirmed. Since both ZnO and (CuZn)O are transparent, nontoxic and abundant, ZnO/(CuZn)O hetrostructure is well suited for transparent and low-cost solar cells. To our knowledge, photovoltaic effects of heterostructure devices based on transparent (CuZn)O has not been reported so far.

2. Experimental details

For ECD, a standard three-electrode cell was used with indium-tin-oxide (ITO)-coated glass substrate as the working electrode. An Ag/AgCl electrode and a platinum sheet were used as the reference electrode and counter electrode, respectively, with Hokutodenko HA151-B potentiostat/galvanostat. The ITO substrates were washed for 5 min in alkyl benzene, acetone and purified water, and the deposited area was $1 \times 1$ cm$^2$. As the bottom layer, p-type (CuZn)O films were fabricated with stirring from an aqueous solution containing 1 mM Cu(NO$_3$)$_2$·3H$_2$O and different concentration of Zn(NO$_3$)$_2$·6H$_2$O (5, 20, 30, and 40 mM). Previously we confirmed that less negative potential is suitable for higher Zn(NO$_3$)$_2$ concentration than for the lower Zn(NO$_3$)$_2$ concentration [25]. Thus, $-0.75\, \text{V}$ was selected as the deposition potential for 5 mM (270 s deposition time) and $-0.7\, \text{V}$ (270 s deposition time) for 20, 30, and 40 mM of Zn(NO$_3$)$_2$. The fabrication bath temperature was RT. All the deposited films were dipped on deionized water and air-dried subsequently. The annealing was carried out at 400 °C in air ambient.
n-type ZnO thin film was deposited by galvanostatic ECD from an aqueous solution containing 100 mM Zn(NO₃)₂ at 60 °C on as-deposited and annealed (CuZn)O in an area of 0.5 × 0.5 cm as the upper layer. The current density was −0.75 mA cm⁻², and the deposition time was 3 min.

Film Thickness values were measurement by an Accretech Surfcom-1400D surface profiler. The compositional analysis of deposited films was done by Auger electron spectroscopy (AES) using a JEOL JAMP-9500F field emission microprobe at a probe voltage of 10 keV. For calculation of Cu/Zn ratios, AES peak-to-peak intensity ratios of Cu and Zn were used. Commercially available standard CuO and ZnO chemicals were used as a reference. Scanning electron microscopy (SEM) images were taken with the magnification of 5000 by using JAMP 9500F. X-ray diffraction (XRD) was investigated by a SmartLab x-ray diffractometer (Rigaku) with a CuKα radiation source. For x-ray photoelectron spectroscopy (XPS), PHI5000 VersaProbe was used with the C₁s peak at 285.0 eV as a reference for correcting the shifts. Optical transmittance measurement was done by using a Jasco V-570 UV/VIS/NIR spectrometer. The ITO substrate was used as a reference. The photoelectrochemical (PEC) experiment was carried out in a three-electrode cell with the Ag/AgCl and deposited films as the reference electrode and working electrode, respectively, and 0.1 M Na₂SO₄ aqueous solution was used as the electrolyte. The potential scan rate was 5 mV s⁻¹. Optical excitation of the films was done by using an Abet Technologies 10500 solar simulator (100 mW cm⁻²) with intermittently-radiated light at 5 s intervals. Indium electrodes of 1 × 1 mm² size were fabricated by vacuum evaporation on the surface, and the current density-voltage (J-V) characteristics were measured under 100 mW cm⁻² (AM1.5) irradiation using a solar simulator as the radiation source.

Figure 5. (a) Optical transmittance spectra of the as-deposited and annealed films, deposited with 1 mM Cu(NO₃)₂ and different Zn (NO₃)₂ concentrations. (b) Plots of (αhν)² versus hν for the annealed samples.
3. Results and discussion

The surface profiler results before and after the annealing show that the thicknesses of all the samples are around 0.15–0.2 μm.

AES results are shown for the as-deposited and annealed samples in Figure 1. All the films exhibited Zn, Cu, and O peaks, as long as a small peak of In. Cu intensity decreases slightly after the annealing.

Figure 2 shows the elemental composition ratio of (CuZn)O films, calculated from the AES spectra. The Cu/Zn ratio for the as-deposited samples deposited from the solution containing 5 mM and 20 mM Zn(NO₃)₂ are 2 and 0.85, respectively while it is 1.3 for 30 mM and 1 for 40 mM Zn(NO₃)₂. For high concentrations of Zn(NO₃)₂, Cu/Zn ratio does not seem to be related to amount of Zn(NO₃)₂. By the annealing, the Cu/Zn intensity ratio decreased slightly to 1.7 for 5 mM Zn(NO₃)₂ whereas there is no considerable change for the other samples (20, 30, and 40 mM).

The SEM images for the as-deposited and annealed samples are presented in Figure 3. In the previous work, it was observed that the grain size of (CuZn)O was smaller and more uniform than for ZnO [25]. There is no meaningful difference in morphology due to annealing or Zn(NO₃)₂ concentration.

The Cu2p XPS core level spectrum of the film deposited with 5 mM Zn(NO₃)₂ is shown in Figure 4. The spectrum of Cu 2p exhibits two strong peaks corresponding to Cu 2p₁/₂ and Cu 2p₃/₂ core levels at around 952.45 eV and 932.5 eV, respectively, and they can be assigned to Cu⁺ oxidation state [19, 30]. This indicates that Cu can act as an acceptor, replacing Zn₂⁺ in ZnO.

XRD was performed for the as-deposited and annealed samples, but no diffraction peaks corresponding to the films were observed. Therefore, all the films are amorphous, even after the annealing at 400 °C. In the previous work, we found that (CuZn)O films deposited at 60 °C exhibited diffraction peaks which can be assigned to ZnO [25]. On the other hand, (CuZn)O deposited as amorphous at RT does not crystallize even at 400 °C.

Figure 5(a) presents the optical transmission for the as-deposited and annealed films deposited with different Zn(NO₃)₂ concentrations. The as-deposited samples have transparency of more than 65% in the visible regions, and after annealing it increased slightly. An obvious absorption edge was confirmed for the annealed films.
whereas for the as-deposited samples, there is no clear absorption edge. The high transparency in the UV range (for photon energies larger than the ZnO band gap) could be related with the formation of Zn(OH)$_2$, or an amorphous ZnO or both [25].

Figure 5(b) shows calculation of the band gap from the plot of $(\alpha h\nu)^2$ versus $h\nu$, where $\alpha$ and $h\nu$ are absorption coefficient and photon energy, respectively. For the as-deposited samples, as the absorption edge does not appear obviously, and thus the band gap cannot be calculated. After annealing, the band gap was found to be between 3.1 and 3.3 eV.

Figure 6 shows the PEC measurement results for the (CuZn)O films. There is clear photo response in the negative part for the as-deposited films, which means that the electron is the minority carrier, i.e., those samples have p-type conductivity. After annealing, a weak positive (n-type) photoresponse was also observed for the samples fabricated with 30 and 40 mM Zn(NO$_3$)$_2$, but the negative (p-type) photoresponse was much larger. In the previous paper, we reported that significant positive photoresponse was observed for (CuZn)O deposited at 60 °C [25]. As noted above, ZnO XRD peaks were observed for the 60 °C-deposited samples, and thus the positive (n-type) response could be due to the ZnO phases. In contrast, (CuZn)O deposited at RT does not exhibit the ZnO XRD peaks and is distinctly p-type even after annealing.

The ZnO/(CuZn)O heterostructures were fabricated by depositing ZnO on the as-deposited and annealed (CuZn)O films. The thickness of the ZnO upper layer is about 100 nm, and the thicknesses of all the heterostructures are approximately 0.3 μm.

Figure 7 shows the optical transmission spectra for the ZnO/(CuZn)O heterostructures. The transmission for all the samples is around 65% in the visible range, and a clear absorption edge is observed. For the as-deposited (CuZn)O single layer, the absorption edge does not appear obviously. Then the absorption edge for the ZnO/(CuZn)O heterostructures (corresponding to a photon energy of approximately 3.4 eV) is due to absorption by ZnO. With annealed (CuZn)O, the absorption edge was shifted to a slightly larger wavelength (approximately 3.2 eV).

The J-V characteristics of the ZnO/as-deposited (CuZn)O heterostructures in the dark and under irradiation are shown in figure 8. For (CuZn)O deposited with 5 mM and 20 mM Zn(NO$_3$)$_2$, rectification and photovoltaic effects were observed, but for the other samples, no photovoltaic effect was confirmed. The parameters derivable from the J-V curves can be found in table 1. It indicates that relatively good values of
open-circuit voltage $V_{oc} = 96$ mV, short-circuit current $J_{sc} = 0.025$ mA cm$^{-2}$, and efficiency $\eta = 6.67 \times 10^{-4}$ have been achieved with 20 mM Zn(NO$_3$)$_2$.

Figure 9 shows rectification and photovoltaic effects for the heterostructure based on annealed (CuZn)O deposited with 20 mM Zn(NO$_3$)$_2$. The parameters are listed in table 2. $V_{oc}$ is very small for (CuZn)O deposited with 5 mM Zn(NO$_3$)$_2$ while $J_{sc}$ is small for 20 mM Zn(NO$_3$)$_2$. No significant photovoltaic effects were confirmed for the other two samples. Thus the annealing did not improve solar cell performance. In the PEC results in figure 6, positive (n-type) response was observed for the annealed (CuZn)O films deposited with 30 and 40 mM Zn(NO$_3$)$_2$. Thus, with annealing and with large Zn(NO$_3$)$_2$ concentration, the film tends to have more n-type or intrinsic character. This could lead to deterioration of the J-V characteristics.

![Image of Figure 8](image.png)

**Table 1.** J-V measurement results for the solar cells with as-deposited (CuZn)O.

| Zn(NO$_3$)$_2$ (mM) | $V_{oc}$ (mV) | $J_{sc}$ (mA/cm$^2$) | FF | $\eta$ (%) |
|---------------------|--------------|---------------------|----|------------|
| 5 mM                | 4.4          | 0.025               | 0.264 | $2.76 \times 10^{-5}$ |
| 20 mM               | 96           | 0.025               | 0.280 | $6.67 \times 10^{-4}$ |
| 30 mM               | 0            | 0                   |     |            |
| 40 mM               | 0            | 0                   |     |            |
Although photovoltaic effects were confirmed for the first time for heterostructures based on (CuZn)O, the photovoltaic conversion efficiency is low. In particular, $V_{oc}$ is very small considering the large band gaps of the constituent materials (more than 3 eV). This can be due to the high density defects at the heterointerface, which can result in large leakage current. Photovoltaic properties may be improved by controlling the structure of the interface.

**Table 2.** J-V measurement results for the solar cells with annealed (CuZn)O.

| Zn(NO$_3$)$_2$ (mM) | $V_{oc}$ (mV) | $J_{sc}$ (mA/cm$^2$) | FF   | $\eta$ (%) |
|---------------------|--------------|----------------------|------|------------|
| 5 mM                | 0.24         | 0.28                 | 0.243| $1.64 \times 10^{-5}$ |
| 20 mM               | 7.7          | 0.011                | 0.252| $2.13 \times 10^{-5}$ |
| 30 mM               | 0            | 0                    |      |            |
| 40 mM               | 0            | 0                    |      |            |
4. Conclusions

In summary, transparent p-type (CuZn)O thin films have been deposited by ECD, and properties of the films have been studied before and after annealing at 400 °C in air. According to XPS, for the as-deposited samples, copper is in the Cu⁺ oxidation state. From the PEC results, conductivity was found to be p-type. On the other hand, for the annealed samples, a weak positive (n-type) response was also observed for the samples deposited with relatively large (30 and 40 mM) Zn(NO₃)₂ concentration. An n-type ZnO/p-type (CuZn)O heterostructures were fabricated for the first time by ECD. Transparency around 65% was revealed in the visible range. The J–V curves of the heterostructure display the characteristics of rectifying diodes, and photovoltaic effects have been confirmed for the first time for the devices based on (CuZn)O.

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