Fabrication of Cu_2O homojunction with ZnO buffer layer

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ABSTRACT

Development of cost effective and efficient solar cells is a priority in studies of renewable energy. Cu_2O comes with a promising photon to electron conversion efficiency of 20% with high absorbance properties as well as non-toxicity. Overall efficiency of Cu_2O based solar cells has been kept quite low compared to the theoretical limit due to the low fill factor and the open circuit voltage of Cu_2O homojunction devices. In this study, a thin layer of ZnO have been deposited in between n-Cu_2O and p-Cu_2O with the expectation of improving the V_{oc} value and the fill factor by acting as a buffer layer which blocks the current flow from n-Cu_2O to p-Cu_2O in operation. Growth of n-type and p-type Cu_2O were carried out by electrodeposition using previously optimized conditions in acetate and lactate baths respectively. Growth of ZnO was done by spin coating using a solution prepared by dissolving zinc acetate dihydrate in methanol. Formation of ZnO on Cu_2O by spin coating technique has been confirmed by HEXRD. The best n-Cu_2O/ZnO/p-Cu_2O device produced V_{oc} of 438 mV, J_{sc} of 8.37 $mAcm^{-2}$, FF of 34.9% and η of 1.28%.

Keywords: Cu_2O electrodeposition, ZnO, Buffer layer, ZnO spin-coating.

1. INTRODUCTION

Cuprous Oxide (Cu_2O) is a low-cost semiconductor material which can be used to fabricate solar cells with efficiencies up to 20%. Having a ~ 2 eV direct bandgap allows Cu_2O to capture the high intensity region of the solar spectrum resulting in high efficiency. Other than combining Cu_2O with another material to form a heterojunction, homojunction solar cells are expected to be more suitable and cost effective [1] [2]. It is reported that the conductivity type of cuprous oxide can be controlled by varying the deposition parameters by electrodeposition technique. To date, the maximum reported efficiency of Cu_2O homojunction solar cells is around 2% which is quite low compared to the theoretical limit. The reason behind this problem is due to the low open circuit voltage followed by low fill factor (FF) (<30%).

Presence of surface states, inherent p-type conductivity of n-Cu_2O, recombination rate are the factors that should be carefully controlled in order to achieve higher V_{oc} values. However, applications or growth of n-Cu_2O is not commonly reported compared to p-Cu_2O in the literature. Therefore, investigations have to be done on perfecting n-Cu_2O thin films to be used in solar cells. In our previous reports, improving the n-type conductivity and eliminating the surface states and fermi level pinning of n-Cu_2O have been investigated [3]. n-Cu_2O was grown on Ti substrates and mitigation of p-type

conductivity was observed with annealing treatments. p-type conductivity of n-Cu_2O thin films were completely eliminated by depositing a thin Cu layer prior to the deposition and annealing at low temperatures for long durations [4]. On the other hand, growth of p-Cu_2O is commonly reported in the literature using various methods such as thermal evaporation, epitaxial growth, chemical bath deposition, thermal oxidation [5]. Most of the reported homojunction devices were fabricated by using electrodeposition technique since it is the only possibility of growth of n-Cu_2O. Uniform p-Cu_2O with high photoresponse were reported by electrodeposition technique in lactate bath in highly alkaline conditions [6].

Fabrication of Cu_2O homojunction as a p-i-n structure with a wide bandgap layer as the intrinsic, could shift fermi energies of n- and p-Cu_2O apart while seizing the unwanted recombination at the junction acting as a buffer layer. Wide bandgap materials such as ZnO, TiO_2, ZnS are commonly reported in literature in heterojunction solar cells as well as organic solar cells [7], [8]. ZnO is a matching buffer layer for Cu_2O where ZnO/Cu_2O heterojunctions are reported commonly [9]. However, in order to fabricate Cu_2O homojunction, the growth of ZnO on top of the n-Cu_2O is quite challenging and not reported previously by anyone to our knowledge to the date. Electrodeposition of ZnO is generally performed in acidic baths [10],[11] in which Cu_2O gets easily dissolved. Similar scenario applies to chemical bath depositions [12]. On the other hand, it is require high temperature annealing to form ZnO which cannot be applied with n-Cu_2O because n-type conductivity of Cu_2O will be hindered by annealing at temperatures beyond 200 ^oC [13] and Cu_2O get oxidized and form CuO at temperatures higher than 400 ^oC [14]. Therefore, in this study, the possibility of growth of ZnO thin films on n-Cu_2O thin film were explored without damaging n-Cu_2O thin film by spin coating technique [15] and thereby fabrication of Cu_2O homojunction. Since the thickness of the ZnO layer plays a key role in this proposed device, it has to be optimized by changing the rpm as well as the solution concentration.

2. EXPERIMENTS AND METHODS

2.1 n-Cu_2O Electrodeposition

Cu_2O thin films were grown on Ti substrates by electrodeposition using a Gamry series 300 Potentiostat / Galvanostat ZRA and a three electrode electrochemical cell having Ti substrate as the working electrode, Pt plate as counter electrode and Ag/AgCl electrode as the reference electrode. Prior to the deposition, Ti substrates were polished with p800, p1200 sandpapers, rinsed with detergent and ultrasonicated in HCl for 15 minutes and finally rinsed with D.I. water thoroughly. Deposition bath was a 100 ml aqueous solution containing 0.1 M sodium acetate and 0.01 M cupric acetate and the pH of the bath was adjusted to be 6.1 by adding diluted acetic acid. Electrodeposition was carried out using the above mentioned setup at the deposition potential of -200 mV with respect to the Ag/AgCl reference electrode. Layer thickness was controlled by limiting the deposited charge to 2 coulombs per cm^2 to obtain 1.6 µm thin n-Cu_2O films. Temperature of the bath was maintained at 55 ^oC while stirring at 50 rev/min with a magnetic stirrer.

2.2 Spin Coating ZnO

ZnO buffer layer was deposited on Ti/n-Cu_2O electrode by spin coating. Deposition solution was prepared by dissolving 1 g of zinc acetate dihydrate in 10 ml of methanol. Solution was stirred for 1 hour and aged for 24 hours before using. Spin coating was carried out at a spinning speed of 2500 rpm for 10 seconds using an Ossila spin coater. Resulted samples were carefully placed in the Carbolite tube furnace for annealing in air in order to remove acetate complexes to form ZnO. Even though the reduction of zinc acetate is reported at high temperatures (>450 ^{0}C), annealing was done at low temperature for a long duration which was 100 ^{o}C for 24 hours followed by 150 ^{o}C for 30 minutes. These annealing conditions were selected for the formation of ZnO as well as optimization of the n-type response of Cu_2O layer.

2.3 p-Cu_2O Electrodeposition

p-Cu_2O thin film was then electrodeposited on annealed samples in a three electrode electrochemical cell containing 0.4 M Copper Sulphate pentahydrate, 4 M Sodium Hydroxide and 2.1 M lactic acid. Deposition potential of -450 mV was applied to Ti /n-Cu_2O working electrode with respect to the Ag/AgCl reference electrode and deposition charge was limited to 0.1 coulombs per cm^2 in order to maintain the thickness of p-Cu_2O film at 0.08 µm. Cu_2O layer thicknesses of the device were selected according to the optimum Ti/n-Cu_2O/p-Cu_2O/Au device fabrication conditions which were carried out previously.

2.4 Sulphiding

After the deposition, samples were rinsed thoroughly with D.I. water and dried in hot air and exposed to 20% ammonium sulphide vapor in order to apply an ultra-thin CuS layer in order to get rid of surface states and create an ohmic contact with Au. The samples having a mask with 8×6 mm opening were exposed to the ammonium sulphide for 8 s by placing the samples 13 cm above the ammonium sulphide container.

2.5 Sputtering Au Contacts

As the final step of sample preparation, Au contacts were grown by sputtering at 10 mA current for 240 s by using 108 Cressington Sputter Coater.

3. RESULTS AND DISCUSSION

3.1 Current-Voltage Measurements

Fabricated devices were characterized by taking current-voltage measurements under illumination of 1.5 AM using Sciencetech SciSun 300 solar simulator. A mask having 4 mm^2 opening was applied on top of the illuminating surface in order to expose a known area of the device. Gamry series G 300 potentiostat/Galvanostat ZRA was used to obtain the measurements and a spring loaded gold probe was used as the contact to the device. As expected, V_{oc} values higher than 400 mV were observed from most of the fabricated devices with J_{sc} values around 8 mAcm^{-2}. However, the current-voltage curves under dark and illumination for the best sample are shown in Fig. 1.

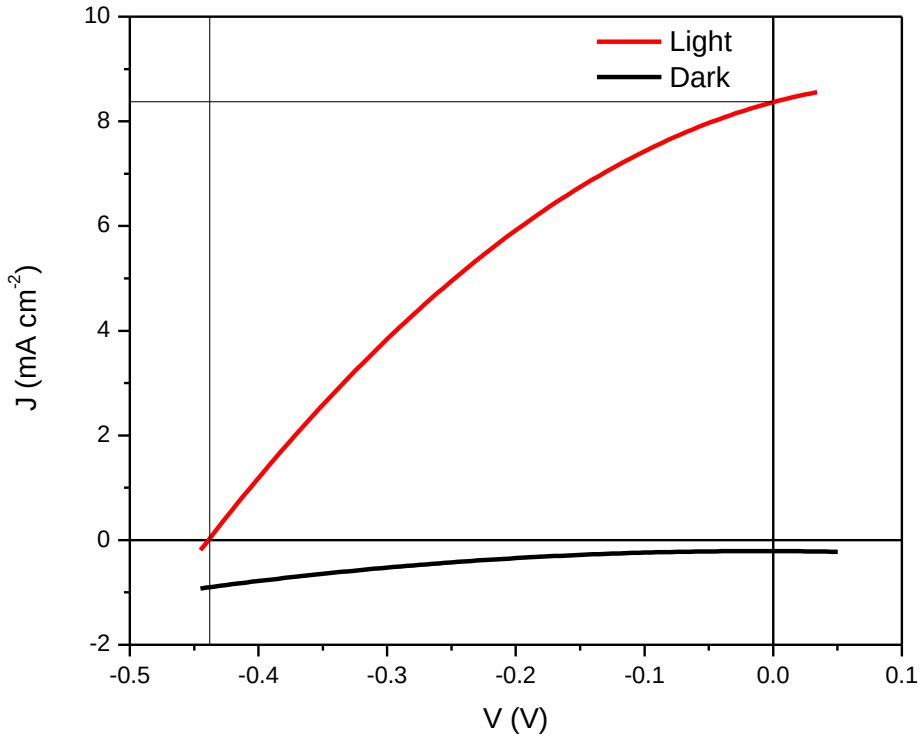

Figure 1. Dear and Light Current-Voltage measurements of Ti/n-Cu_2O/ZnO/p-Cu_2O/Au device under AM 1.5 illumination.

Device shown in Fig. 1 exhibited V_{oc} of 438 mV and J_{sc} of 8.37 mAcm^{-2} with a FF of 34.9% resulting an efficiency (η) of 1.28%. Although these results are low compared to the best device fabricated without introducing ZnO to the homojunction, these findings are encouraging because still significant photoresponse is produced by the device after introducing ZnO. The best Ti/n-Cu_2O/p-Cu_2O/Au device produced V_{oc} of 445 mV, J_{sc} of 12.95 mA cm^{-2}, FF of 39.5% and η of 2.28%. When comparing the results of two devices, the value of J_{sc} reduced from 12.95 to 8.37 mAcm^{-2}. In this present investigation, it was expected to improve the V_{oc}, FF and η values of the device with the introduction of ZnO buffer layer while preserving the resulted high J_{sc} value. In order to penetrate photogenerated elections from p-Cu_2O to n-Cu_2O and holes from n-Cu_2O to p-Cu_2O without trapping, the thickness of the ZnO layer is crucial and there should be few atomic layer thick layers. Therefore, the thickness of the ZnO layer has to be carefully controlled to achieve the goal.

3.2 Structural Characterization

Prepared samples were characterized by HEXRD measurements to confirm the growth of ZnO on Cu_2O. Two samples of n-Cu_2O and n-Cu_2O/ZnO were prepared and Cu_2O and Cu_2O/ZnO layers were peeled off and put inside a capillary tube and scanned with high energy X-rays at wavelength of 0.49592 Angstrom. As shown in Fig. 2, curve (a) is the

XRD pattern of the n-Cu_2O sample where the curve (b) represents the XRD pattern of the n-Cu_2O/ZnO bi-layer. All the XRD peaks shown in curve (a) are corresponding reflections of n-Cu_2O planes indicating the growth of single phase n-Cu_2O. The XRD pattern of the curve (2) shows the existence of three peaks in addition to the Cu_2O peaks. These three peaks are corresponding reflections of ZnO material confirming the successful growth of ZnO on n-Cu_2O. Peaks corresponding to Cu_2O are quite clearly visible in both samples however ZnO produces very low intensity peaks indicating the formation of a very thin ZnO layer compared to the Cu_2O.

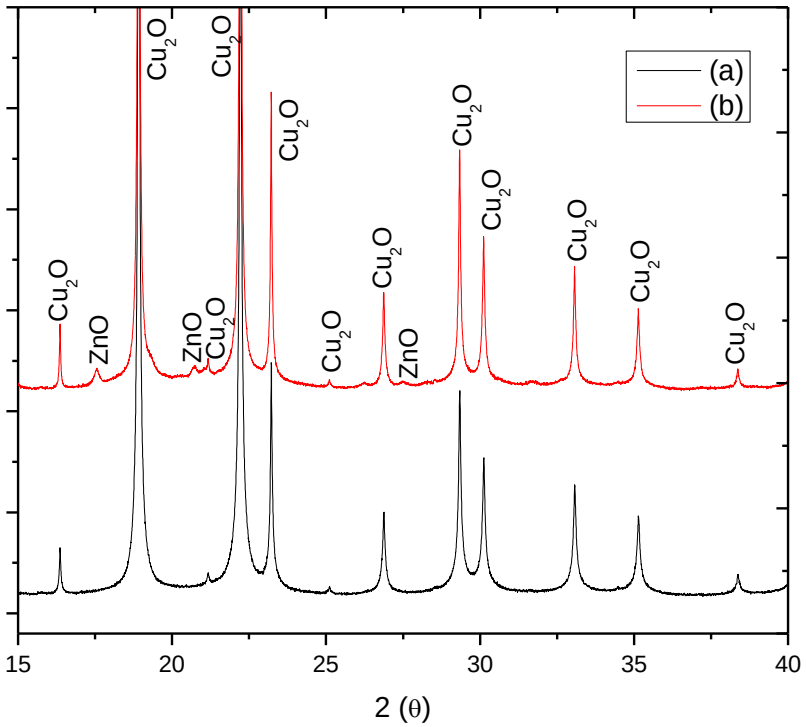

Figure 2. HEXRD measurements of (a) n-Cu_2O annealed at 100 ^oC for 24 hours and (b) n-Cu_2O/ ZnO annealed at 100 ^oC for 24 hours.

This preliminary investigation produced encouraging results on fabrication of Cu_2O homojunction with the introduction of ZnO buffer layer in between two Cu_2O layers. However, to achieve the goal, further investigations are required to improve the quality of the ZnO layer and optimization of thickness of the ZnO layer.

4. CONCLUSION

In this study, possibility of fabrication of Cu_2O homojunction with the introduction of ZnO buffer layer in between two Cu_2O layers has been investigated and results revealed that it is possible to fabricate photoactive Cu_2O homojunction with the deposition of ZnO buffer layer by spin coating technique. HEXRD characterizations confirmed the growth

of single phase ZnO on n-Cu_2O. Best device produced V_{oc} of 438 mV, J_{sc} of 8.37 $mAcm^{-2}$, FF of 34.9% and η of 1.28%. However, J_{sc} value of the device reduced from 12.95 to 8.37 $mAcm^{-2}$ when compared to the Cu_2O homojunction without ZnO buffer layer. Optimization of growth conditions and the thickness of the ZnO layer are required to improve the photoactive performance of the device.

5.ACKNOWLEDGEMENT

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