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Electrodeposited CuO/Cu_2O heterojunction for PV applications

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ABSTRACT

Anodic electrodeposition was carried out to grow CuO thin films on Ti substrate at a deposition potential of 700 mV vs. SCE in an aqueous solution containing 0.4 M $CuSO_4$ and 3.0 M lactic acid. CuO thin films were annealed at 375 ^{o}C for 15 min in air to improve the surface quality prior to the growth of Cu_2O films, in order to fabricate the heterojunction. After growth of n-Cu_2O, zero bias spectral response and dark and light I-V characteristics in PEC were employed to investigate n-Cu_2O growth conditions on p-CuO thin films. CuO/Cu_2O heterojunction solar cells were fabricated by electrodeposition of n-Cu_2O thin film on Ti/CuO electrode at -200 mV vs. SCE for 60 min in an acetate bath. $Ti/CuO/Cu_2O/Au$ solar cell structure was characterized using zero bias spectral response and dark and light I-V characteristics and the cell produced V_{OC} of 290 mV and I_{SC} of 2.63 mA/cm^2.

1. INTRODUCTION

Photovoltaic (PV) is one of the most promising devices to overcome the problem associated with primary energy sources. Therefor a major concern has been developed today to explore low cost PV materials to reduce the cost of the PV devices. On the other hand commonly used Si solar cell devices are reaching their maximum efficiency and they are still very costly. Copper Oxides, cuprous oxide (Cu_2O) and cupric oxide (CuO), are attractive materials for PV application due to their suitable optoelectonic properties, low cost and non-toxicity [1, 2]. CuO is a p-type direct bandgap material of 1.2 eV which is suitable as an absorber material for solar radiation [1] while Cu_2O having a direct bandgap of 2 eV is suitable as window material [3, 4] for PV devices. Both materials are native defect type semiconductors. Possibility of fabrication of CuO/Cu_2O heterojunction solar cell has been reported in 2010 [5]. In the reported study, p-CuO thin films were grown on Ti substrate by annealing electrodeposited Cu_2O in air and n-Cu_2O thin films were electroeposited on CuO to fabricate CuO/Cu_2O heterojunction solar cell. Recently, the possibility of fabrication of heterojunction of CuO/Cu_2O using a different methodology has been reported [6]. However, photoactive performance of the device reported so far were very poor compared to the theoretical limits. Therefor it is very important to further investigate CuO/Cu_2O heterojunction by changing the growth technique and conditions for improving the device performance. In the present study, direct electrodiposition of both CuO and Cu_2O films were carried out to fabricate CuO/Cu_2O heterojunction solar cell. Growth conditions were investigated by employing linear sweep voltammetry curves and $Ti/CuO/Cu_2O/Au$ heterojunction was characterized using dark and light I-V and spectral responses measurements.

2. EXPERIMENTAL

Anodic electrodeposition of CuO on Ti substrate was potentiostatically carried out in a three electrode electrochemical cell containing 0.4 M $CuSO_4$ and 3.0 M lactic acid aqueous solution. Counter and reference electrodes were a platinum plate and a SCE respectively. The pH of the bath was adjusted by adding 4.0 M NaOH. The temperature of the bath was maintained at 60 ^{o}C and the electrolyte was continuously stirred using a magnetic stirrer. Prior to the deposition of Cu_2O,Ti substrates were polished with sand paper and cleaned with detergent, dilute HCl, distilled water and finally ultrasonically. Electrolytic solutions were prepared with distilled water and reagent grade chemicals. Electrodeposition potential was investigated by studying linear sweep voltammetry curves at different pH of the bath. CuO thin films were eletrodeposited at 700 mV vs. SCE by adjusting the pH value of the bath to 12.5 to fabricate CuO/Cu_2O heterojunction. After the deposition, Ti/CuO films were rinsed with distilled water and dried in air. In order to fabricate CuO/Cu_2O heterojunction, Cu_2O thin film was electrodeposited on Ti/CuO thin film electrodes at different deposition potential of -200 mV to -500 mV vs. SCE in acetate bath containing 0.1 M sodium acetate and 0.01 M cupric acetate aqueous solutions. Optimum growth conditions of Cu_2O on Ti/CuO thin film were studied using zero bias spectral response in a PEC containing 0.1 M sodium acetate. I-V and spectral response measurements in the PEC were obtained to investigate the formation of CuO/Cu_2O heterojunction. Front contact to the CuO/Cu_2O heterojunction was prepared by sputtering an Au grid on top of the Cu_2O film. Ti/ CuO/Cu_2O/Au cell was characterized using dark and light I-V and spectral response measurements. The spectral response of the electrode was measured using a phase sensitive detection method to monitor the photocurrent signal produced by a chopped monochromatic light beam. The chopping frequency was 60 H_Z. A computer interfaced monochromator (Sciencetech – 9010), a potentiostat (Computer integrated Gamry Series G 300) a lock-in amplifier (Stanford Research – SR 830 DSP) and a chopper (Stanford – SR 540) were used for the spectral response measurements. Au was sputtered using Cressington 108 Auto sputter coater.

3. RESULTS AND DISCUSSION

Fig. 1 shows the linear sweep voltammetry curves obtained in the electrolyte containing 0.4 M $CuSO_4$ and 3.0 M lactic acid at different pH values of 9, 10, 12 and 13. At the pH 9 and 10 anodic peaks was obtained at the potential around 1.1 V vs. SCE while it was shifted to around 700 mV vs. SCE when the pH of the bath was increased to 13. This anodic peak current at anodic potentials indicate the formation of CuO in the presence of Cu^{2+} ions in the bath. Deposition potential of 700 mV vs. SCE and 12.5 pH of the bath were selected to grow CuO and deposited films were black coloured CuO. Lower anodic potential was selected for the deposition of CuO films because at higher potentials hydroxides are formed. 15 min deposition is sufficient to obtain well covered CuO thin film on Ti substrate. During the deposition, the color of bath was also changed from dark blue to black.

In order to fabricate the CuO/Cu_2O heterojunction, deposition of n-Cu_2O on Ti/CuO, in acetate bath by employing different electrolytic conditions and deposition potentials, were tested. However, it was unable to deposit Cu_2O on as grown CuO films. Therefore,

electrodeposition of Cu_2O in acetate bath was tested on CuO films after annealing at different temperatures and durations. Well covered Cu_2O thin film were able to grow in an electrolyte containing 0.1 M sodium acetate and 0.01 M cupric acetate aqueous solutions at -200 mV vs. SCE on the CuO films obtained after annealing at 375 ^{o}C for 15 min in air. According to our result, surface quality of CuO after annealing at 375 ^{o}C for 15 min in air may be favorable for growing Cu_2O, but it is not certain at this stage and it will be subject for our future investigation.

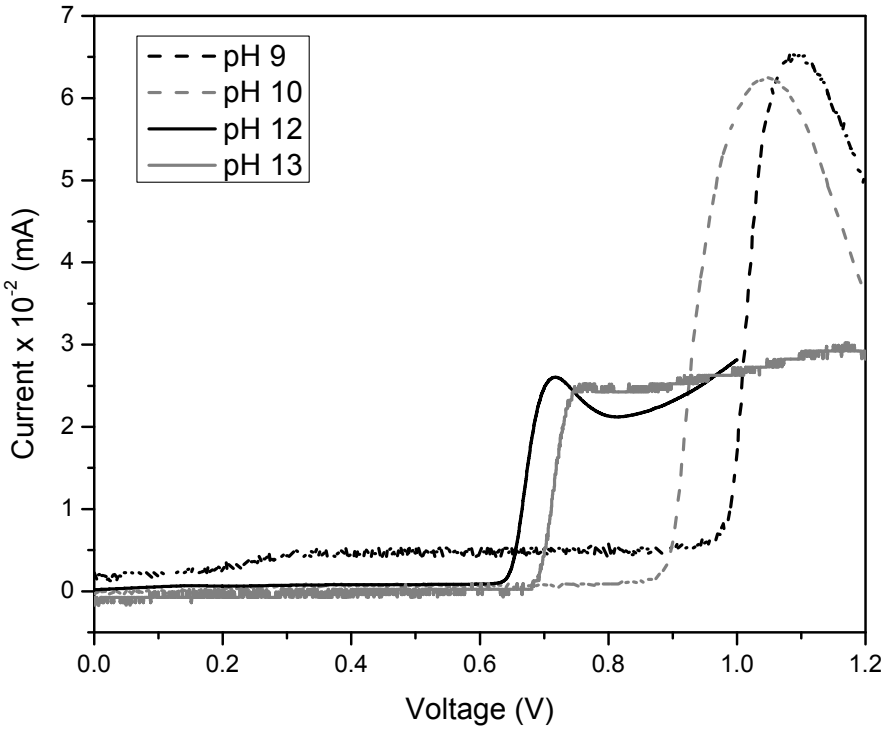

Fig. 1: Linear sweep voltammetry curves on the Ti substrate obtained in a solution containing 0.4 M $CuSO_4$ and 3.0 M lactic acid for different pH values of 9, 10, 12 and 13

To investigate the growth of n-type Cu_2O on CuO dark and light I-V characteristics of Ti/CuO/Cu_2O photoelectrode was studied in PEC containing 0.1 M sodium acetate. As shown in Fig. 2, anodic photocurrent generates when the bias potential is scanned from 50 mV to -220 mV vs. SCE and anodic photocurrent changed to cathodic photocurrent for more negative bias potentials than -220 mV vs. SCE. This results suggest the formation of two barriers in the Ti/CuO/Cu_2O/electrolyte system. Anodic photocurrent is produced by Cu_2O/electrolyte interface while cathodic photocurrent is produced by CuO/Cu_2O interface. Therefore this result reveals the growth of n-Cu_2O on CuO and formation of CuO/Cu_2O heterojunction. At zero bias, resultant photocurrent is anodic indicating the Cu_2O/electrolyte interface dominate the photocurrent of Ti/CuO/Cu_2O/electrolyte system.

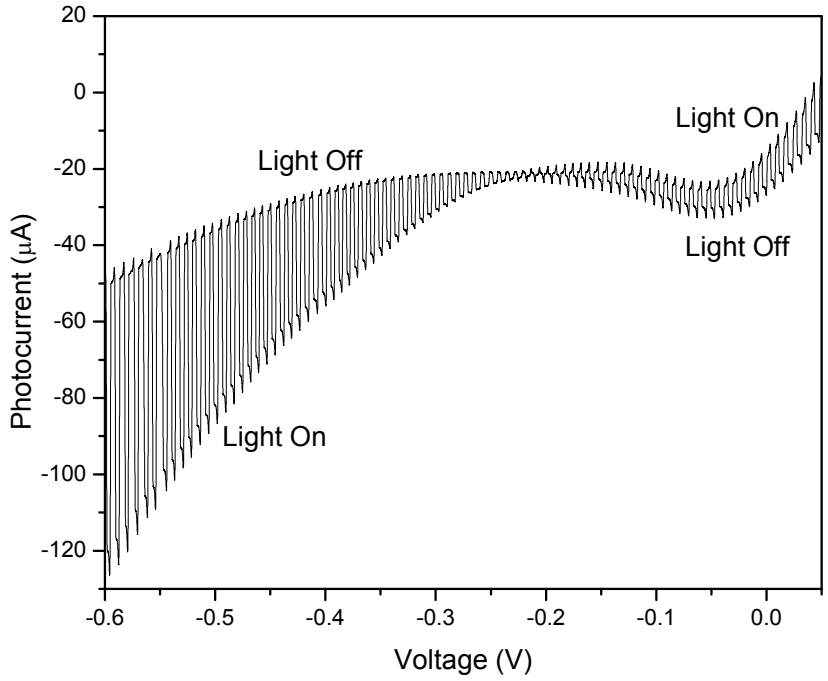

Fig. 2: Dark and light I-V characteristic obtained for Ti/CuO/Cu_2O electrode in PEC containing 0.1 M sodium acetate electrolyte

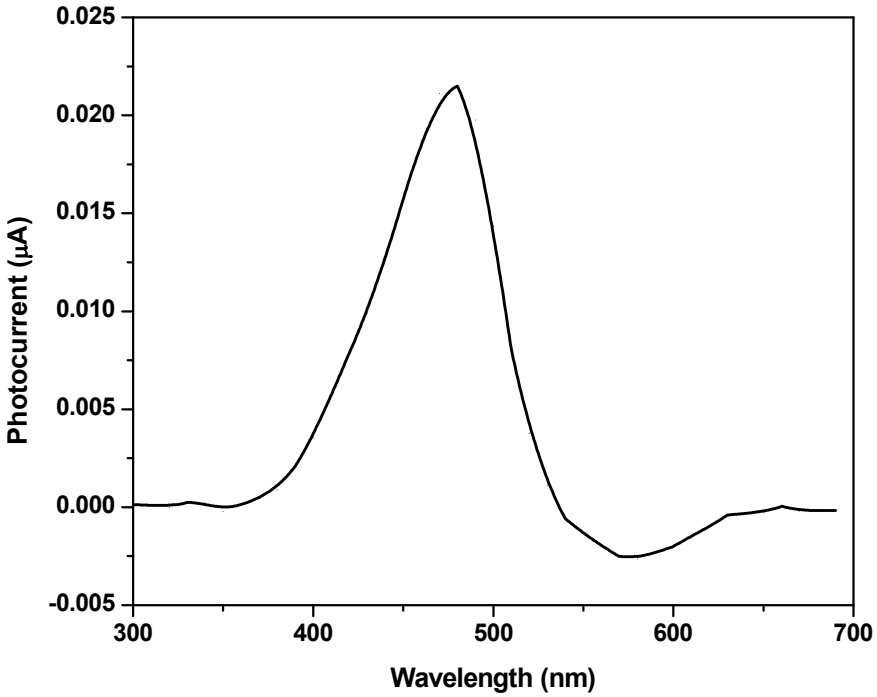

Fig. 3: Spectral response measurement obtained for Ti/CuO/Cu_2O electrode in PEC containing 0.1 M sodium acetate electrolyte

This was further investigated by employing zero bias spectra response of the Ti/CuO/Cu_2O/electrolyte system. Fig. 3 shows the spectral response measurement of Ti/CuO/Cu_2O electrode in 0.1 M sodium acetate electrolyte. n-type photosignal generated for the shorter wavelengths from 350 to 530 nm while small p-type photocurrent given for the long wavelengths from 530 to 670 nm. Short wavelength produce photogenerated electron hole pairs at the surface of the device while longa wavelength produce photogenerated electron hole pairs in the interior of the device since penetration depth of the longer wavelength is higher than short wavelength. Dominant n-type signal reveals that the formation of anodic barrier between Cu_2O and electrolyte indicating the growth of n-Cu_2O on CuO. The small p-type signal for longer wave lengths suggest that the net oppositely driven charge carriers are generated at the interior of the CuO/Cu_2O junction comparing with the charge separation at the front Cu_2O and electrolyte interface. Results further revealed that the band gap energy of electrodeposited CuO is ~1.85 eV which is higher than the ideal CuO band gap energy of 1.2 eV. However, it is important to note that photoactivity of the Ti/CuO/Cu_2O heterojunction can be further improved by using proper ohmic contact to n-Cu_2O.

Ti/CuO/Cu_2O/Au structure was fabricated by sputtering Au grid on the Cu_2O surface as shown in the Fig. 4. Fig. 5 shows the dark and light I-V characteristic of the Ti/CuO/Cu_2O/Au hetrojunction solar cell. As shown in the I-V characteristic, Ti/CuO/Cu_2O/Au structure exhibits only p-type photocurrent attributing the formation of single barrier of CuO/Cu_2O. Results suggest that the dominant junction is the CuO/Cu_2O hetrojunction and Au makes a near ohmic contact with n-Cu_2O. This is further investigated by employing the spectral response measurements. Fig. 6 shows the zero bias spectral response of the Ti/CuO/Cu_2O/Au hetrojunction solar cell. As shown in Fig. 6, small n-type photosignal is generated for short wavelengths while dominant p-type photosingal is generated for long wavelengths. Generation of small n-type signal suggest that the formation of small n-type Schottky barrier at Cu_2O/Au junction. Therefore this results reveal that Au produces nonohmic contact with n-Cu_2O and photoactivity of p-CuO/n-Cu_2O heterojunction can be further improved by choosing proper ohmic contact with n-Cu_2O. In our investigation, best Ti/CuO/Cu_2O/Au hetrojunction solar cell produced V_{OC} of 290 mV and I_{SC} of 2.63 mA/cm^2. On the other hand it has been reported that the surface passivation of n-Cu_2O by ammonia enhance the photoactivity of the Cu_2O hormojunction solar cell [7, 8]. Therefor similar approach might be useful to enhance the photovoltaic properties of the CuO/Cu_2O hetrojunction and this will be a subject for our future investigation.

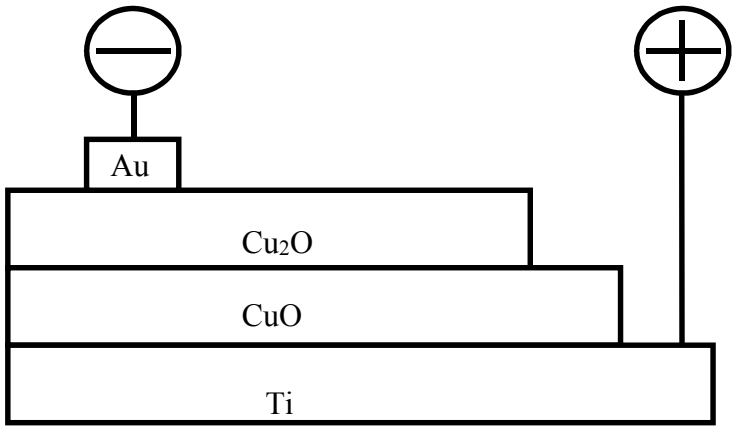

Fig. 4: Ti/CuO/Cu_2O/Au heterojunction solar cell

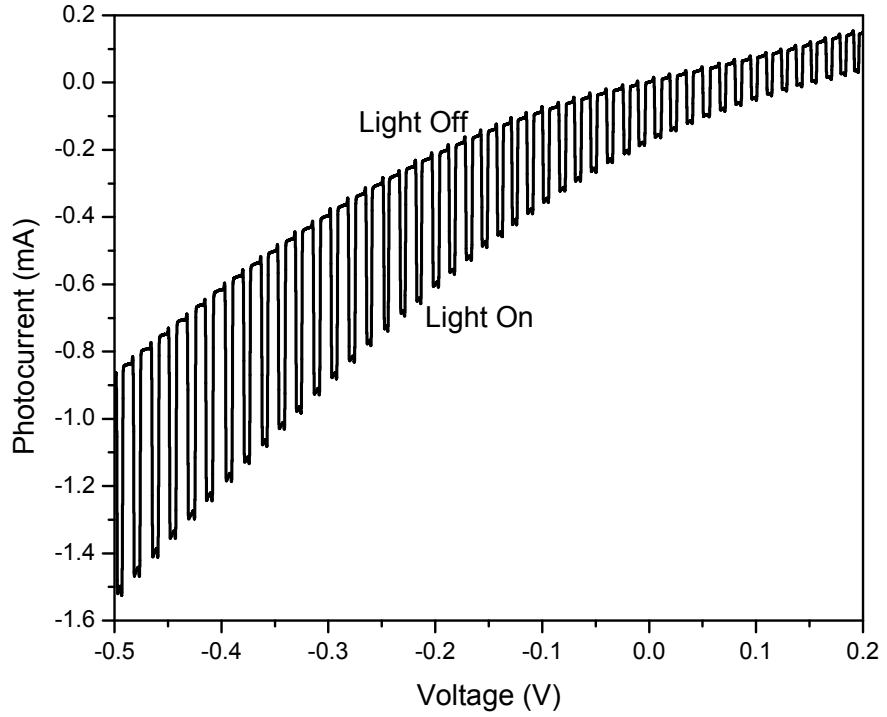

Fig. 5: Dark and light I-V characteristic of Ti/CuO/Cu_2O/Au hetrojunction solar cell

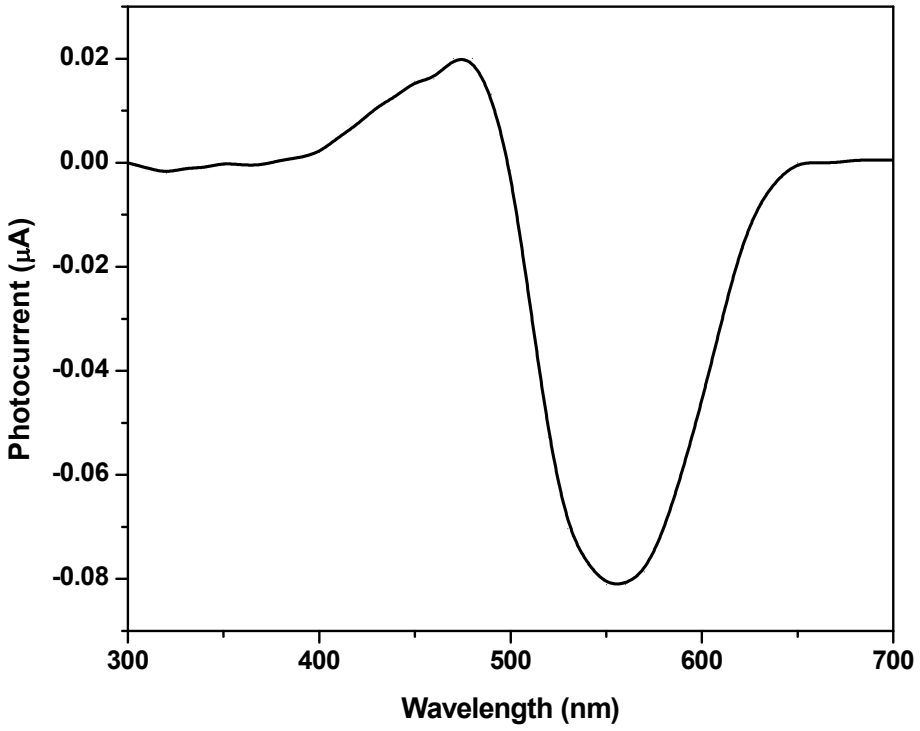

Fig. 6: Spectral response measurement of Ti/CuO/Cu_2O/Au heterojunctin solar cell

4. CONCLUSION

Photoactive p-CuO thin films can be electrodeposited at 700 mV vs. SCE in the electrolyte containing 0.4 M $CuSO_4$ and 3.0 M lactic acid. Well covered n-Cu_2O thin films can be electrodeposited at -200 mV vs. SCE in the electrolyte containing 0.01 M cupric acetate and 0.1 M sodium acetate on post annealed CuO thin films. In this study, best Ti/CuO/Cu_2O/Ag heterojunction solar cell produced V_{OC} of 290 mV and I_{SC} of 2.63 mA/cm^2. Further, results reveal that Au produces nonohmic contact with n-Cu_2O and performance of the CuO/Cu_2O heterojunction solar cell can be further improved by producing a proper ohmic contact with n-Cu_2O.

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