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Fabrication of an Efficient Cu_2O Homojunction by ElectrodepositionTechnique for Solar Cell Applications

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ABSTRACT

Electrodeposition is a very attractive low cost technique for fabrication of Cu_2O homojunction solar cells. Although electrodeposited p-n homojunction Cu_2O(metal substrate/p-Cu_2O/n-Cu_2O) solar cells were reported earlier, n-p homojunction Cu_2O(metal substrate/n-Cu_2O/p-Cu_2O) solar cellsare very limited in the literature. This solar cell structure is very important when exploring the possibilities to improve the efficiencies of reported Cu_2O homojunction solar cells.In this study, current-voltage characteristics and spectral response measurements were employed to investigate the possibilities of fabrication of n-p homojunction Cu_2O solar cell by electrodeposition technique. Different deposition conditions were adopted to grow and optimize the p-type and n-type Cu_2Ofilms.n-Cu_2O thin films were electrodeposited on Ti substrate using an acetate bath of pH 6.1,where the resulted filmsproduced only the n-type photoresponse in a PEC.Subsequently, ap-Cu_2O thin film was elecrodeposited on Ti/n-Cu_2O electrode usingan acetate bath with acupric ion concentration of 0.001 M. This study revealed the possibility of fabrication of an efficient n-p homojunction of Cu_2O for the applications insolar cells by consecutive electrodeposition of ann-Cu_2Ofilm followed by a p-Cu_2O filmusingan acetate bath.

1.0 INTRODUCTION

Cuprous oxide (Cu_2O) is an attractive material for photovoltaic applications due to its unique properties[1-6]. It is a defect type semiconductor and it is well established as a p-type material due to the Cu vacancies created in the crystal lattice[7-12]. However, it has been reported earlier that n-Cu_2O films can be deposited using the electrodeposition technique[13]. Origin of the n-type conductivity of Cu_2O is considered as due to the excess of Cu ionsand/or O vacanciescreated in the Cu_2O lattice. In general, conductivity type in electrodeposited Cu_2O films strongly depends on the pH and cupric ion concentration of the depositing bath solution[14-15]. Acidic baths produce n-type films while basic baths produce p-type films. However, electrodeposition technique of Cu_2O is very attractive because ofits simplicity, low cost andlow-temperature process. Indeed, control of deposition parameters of the bath to produce n-Cu_2O or p-Cu_2O thin films having better optoelectrical properties is very important for them to be used in solar cell applications.

Many authors have reported the possibility of the p-n homojunction Cu_2O (metal substrate/p-Cu_2O/n-Cu_2O)solar cells[14,16-18].However, to our knowledge, fabrication of n-phomojunction Cu_2O (metal substrate/n-Cu_2O/p-Cu_2O)solar cells using only acetate bathhas not been reported earlier although *Jayathilakaet. al.*[19] has reported the possibility of fabrication of similar solar cell using acetate and lactate baths for growth of n-Cu_2O and p-Cu_2O respectively.The reason may be that during the growth of p-type filmon an n-Cu_2O film using a high pH bath, type conversion in n-type film couldoccur resulting a very poor homojunction. Indeed, fabrication of n-phomojunction Cu_2O is very important due to the availability of many ohmic contact materials to p-Cu_2O than n-Cu_2O.Also, it provides an opportunity to explore various cell structures for the development of Cu_2O homojunction solar cells. In this investigation, various deposition conditions have been tested to obtain and to optimize the photoactive properties of the n- and p-Cu_2Othin films on Ti substrate. Thereby n-p homojunctionofCu_2O was fabricated using two step electrodeposition of n-Cu_2O followed by p-Cu_2O on Ti substratein an acetate bath. Ti/n-Cu_2O/p-Cu_2O homojunctions were characterized using current-voltage characteristics and spectral response measurements in PEC. Results revealed the possibility of fabrication ofn-Cu_2O/p-Cu_2O homojunction solar cells.

2.0 EXPERIMENTAL

Cu_2O thin films were potentiostatically electrodeposited on Ti substrates in a three electrode electrochemical cell containing an aqueous solution of sodium acetate and cupric acetate. Counter and reference electrodes were a platinum plate and an Ag/AgCl electrode respectively. The temperature of the electrolyte was maintained at 55 ^{o}C. Different deposition baths were tried by changing the cupric acetate concentration and pH of the bath. pH value (5.50 to 7.50) of the bath was adjusted by adding dilute hydrochloric acid or sodium hydroxide. Prior to the film deposition substrates were cleaned with detergent and ultrasonicated diluted HCl and distilled water. Electrolytic solutions were prepared with distilled water and reagent grade chemicals. After the film deposition, electrodes were immediately washed in distilled water anddried in air.

n-Cu_2O thin film was elecrodeposited on a Ti substrate at -200 mV Vs Ag/AgCl for 60 min in a 0.1 M sodium acetate and 0.01 M cupric acetate aqueous solution. pH of the bath was adjusted to 6.12 by adding diluted HCl. In order to fabricate n-p homojunction Cu_2O solar cell, p-Cu_2O thin film was elecrodeposited on Ti/n-Cu_2O electrode at -200 mV Vs Ag/AgCl for 40 min in a 0.1 M sodium acetate and 0.001 M cupric acetate aqueous solution.

Cu_2O thin films and n-p homojunctionCu_2O solar cells were characterized in a three electrode photoelectrochemical cell (PEC) containing a 0.1 M sodium acetate aqueous solution. The counter electrode was a platinum plate and the reference electrode was the Ag/AgCl. The dark and light current–voltage characteristics and zero biased spectral response measurements were used to optimize n- and p-Cu_2O thin films. Formation of the n-p homojunctionCu_2O solar cell was investigated bythe spectral response measurements and dark and light current–voltage characteristics in a PEC.The dark and light current–voltage characteristics of the samples were simultaneously measured by chopping the white light (1.5 AM) and thespectral response measurements of the films in the same PEC were obtained using a phase sensitivedetection method to monitor the photocurrent signal produced by a chopped monochromaticlight beam at chopping frequency of 53 Hz. The experimental set-up consistedof a lock-in amplifier (Stanford Research-SR 830 DSP), a potentiostat (HukotoDonko HAB-151), a monochromator

(Sciencetech - 9010) and a chopper (Stanford-SR 540).The surface morphology of the Cu_2O thin films was studied by the scanning electron micrographs (SEM) and the bulk structure of the n-p Cu_2O homojunction was studied by X-ray diffraction (XRD) measurements.

3.0 RESULTS AND DISCUSSION

Fig. 1 shows the dark and light current-voltage characteristics of a Cu_2O thin film electrode which was grown potentiostatically at -200 mV Vs Ag/AgCl in 0.1 M sodium acetate and 0.01 M cupric acetate solution of pH 6.5. It is clear in Fig. 1, an anodic (n-type) photocurrent generates at zero bias and increases with increasing anodic potential, indicating the n-type photoconductivity due to the anodic potential barrier formed at the semiconductor/electrolyte interface. The anodic photocurrent decreases with increasing cathodic potential and reaches zero at -330 mV Vs Ag/AgCl and inverts to a cathodic photocurrent. This photocurrent inversion is common to most of the reported n-Cu_2O thin films.However, this additional p-type photoresponse along with the dominant n-type behavior causes a major problem for the application of these films in solar cell devices, as they reduce the overall performance of the devices.

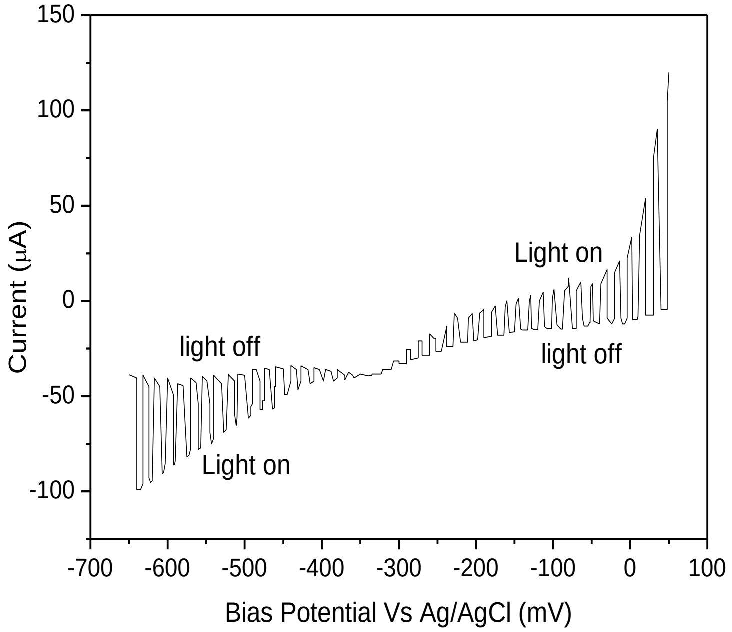

Fig. 1: Dark and light current-voltage measurements of Cu_2O thin film grown at pH 6.5in a PEC containing 0.1 M sodium acetate solution

In this study, photoresponse of the Cu_2O thin films which were prepared by adjusting the pH of the deposition bath wasinvestigated in a PEC containing 0.1 M sodium acetate.pH values of the baths were adjusted by adding dilute hydrochloric acid or sodium hydroxide solutions.Fig. 2 shows the dark and light current-voltage characteristics of the Cu_2O thin film grown at pH 6.1.As revealed by the I-V measurements, n-type photoactivity of Cu_2O thin films improves significantly due to the completely removal of p-type photoactivity when the films were grown at pH 6.1. Results show that pH of the bath is a crucial parameter in obtaining Cu_2O films producing only n-type photoresponse. Above resultswerefurther investigated by employing zero bias spectral response measurements in a PEC containing 0.1 M sodium acetate aqueous solutions. Fig. 3 shows the spectral response of the Cu_2O gown at pH 6.5 and 6.1. Spectral response spectrumobtained for the film grown at pH 6.5 exhibits the n-type photocurrent for short wavelengthsand p-type photocurrent for long wavelengths indicating the formation of

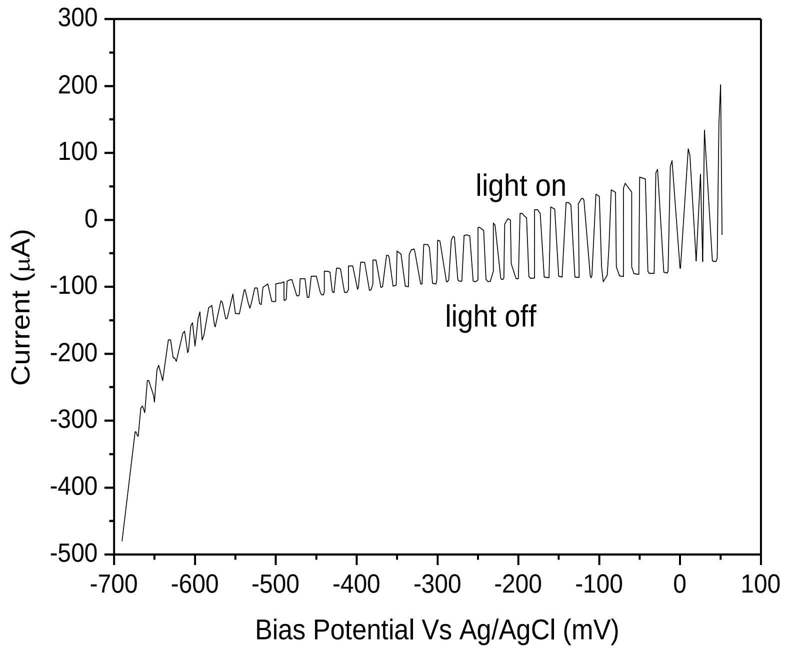

Fig.2: Dark and light current-voltage measurements of Cu_2O thin film grown at pH 6.1 in a PEC containing 0.1 M sodium acetate solution

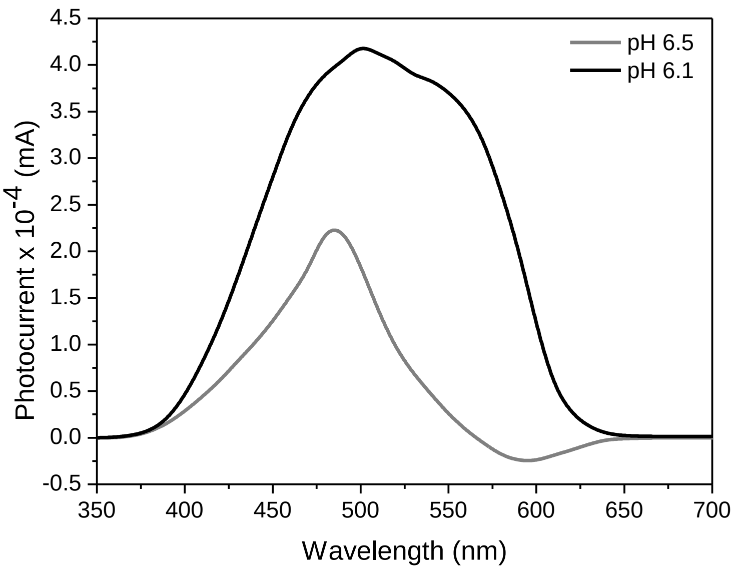

Fig.3: Spectral response measurements of Cu_2O thin filmsgown at pH 6.5 and 6.1 in a PEC containing 0.1 M sodium acetate solution

p-n duplex layers, as the longer wavelengths have larger absorption depths than the shorter wavelengths. However, spectral response of the Cu_2O grown at pH 6.1 produces only n-type photocurrent in the entire spectral range indicating the formation of a good n-Cu_2O film.This result is in good agreement with the photoactivity improvement shown by the I-V characteristics.

Fig. 4 shows the scanning electron micrographs of n-Cu_2O thin films. It is evident that the Cu_2O thin films grown on Ti substrates are uniform and polycrystalline. The observed Cu_2O thin films exhibit cubic structure with a crystal size of 500 nm.

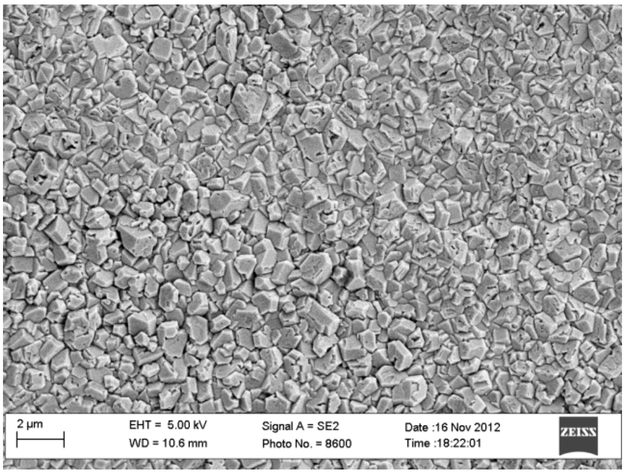

Fig.4: Scanning electron micrographs of n- Cu_2O thin films

In this investigation p-type films were deposited using an acetate bath having very low cupric ion concentration. The main intention was to avoid baths having high pH values, such as lactate baths with high pH values that give poor homojunctions when p-type films are deposited on n-type films.Indeed, it can be expectedthat growth of a p-Cu_2O film by lowering the Cu^{++} ion concentration of the deposition bath, becausep-type conductivity attributed to the formation of Cu vacancies created in the Cu_2O lattice. In this respect Cu_2O thin films were electrodeposited on Ti at -200 mV Vs Ag/AgCl for 60 min in a 0.1 M sodium acetate and 0.001 M cupric acetate aqueous solution.This is a novel approach that we have tested in this investigation to electrodeposit p-Cu_2O film on an n-Cu_2O film to create a homojunction.Fig. 5a shows the dark and light current-voltage characteristics of a Cu_2O thin film prepared at 0.001 M Cu^{++} ion concentration in a PEC containing 0.1 M sodium acetate solution.I-V characterization demonstrates that the cathodic photocurrent is generated at zero bias and is increased with the increasing of cathodic potential. Results indicate the p-type photoconductivity due to the cathodic potential barrier formed at the semiconductor/electrolyte interface. This was further studied with the spectral response spectrum in PEC as shown in Fig. 5b. Spectral response of the Cu_2O grown at 0.001 M Cu^{++} ion concentration produces only p-type photocurrent in the entire spectral range indicating the formation of a good p-Cu_2O film.Indeed, introduction of low Cu^{++} ion concentration in the bath favors the growth of Cu vacancies in the Cu_2O lattice causing the growth of p-Cu_2O[14].n-phormojunctionof Cu_2O was fabricated using sequential electrodeposition of n-Cu_2O followed by p-Cu_2O.

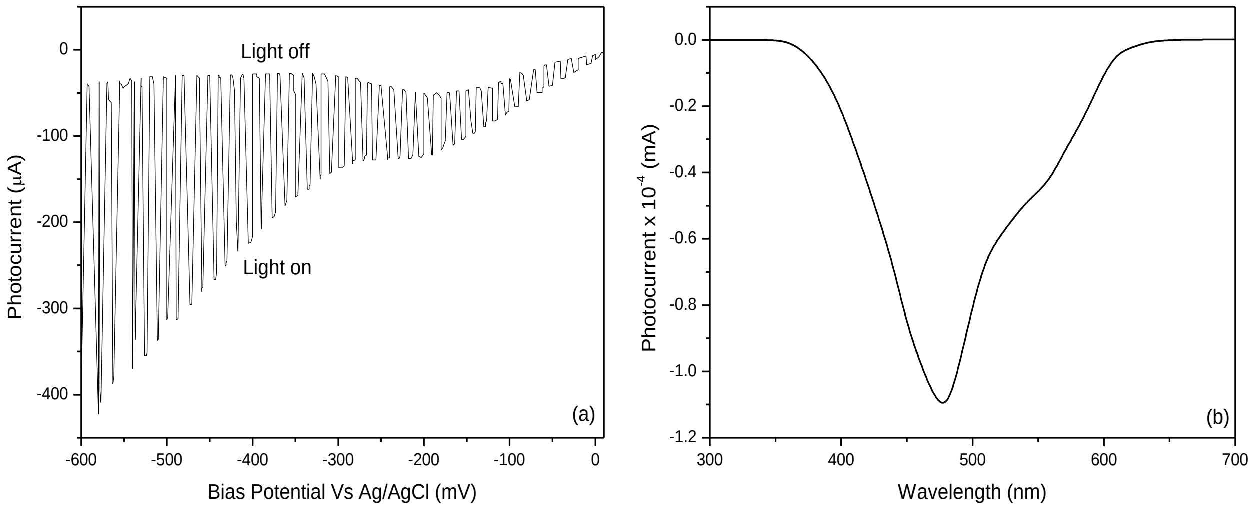

Fig.5: (a) Dark and light current-voltage measurements (b) Spectral response measurements of a Cu_2O thin film prepared at 0.001 M Cu^{++} ion concentration, in a PEC containing 0.1 M sodium acetate solution

In order to fabricate n-p hormojunction, n-Cu_2O was deposited at pH of 6.12 on the Ti substrate for 60 min. Films were annealed at 100 ^{o}C for 24 hours in air to improve the n-type photoactive performance and then p-Cu_2O was deposited directly on to the n-Cu_2O film at 0.001 M Cu^{++} ion concentration for 40 min. In this study, current-voltage characteristics and spectral response measurements were employed to investigate the possibilities to fabricate n-p homojunction. Fig. 6 shows the dark and light I-V characterisation of the n-p hormojunction in the PEC containing 0.1 M sodium acetate. Cathodic photocurrent produces at zero bias and reduce to zero at around -650 mV Vs Ag/AgCl indicating that the photoresponse generated by then-p hormojunction. Asthe

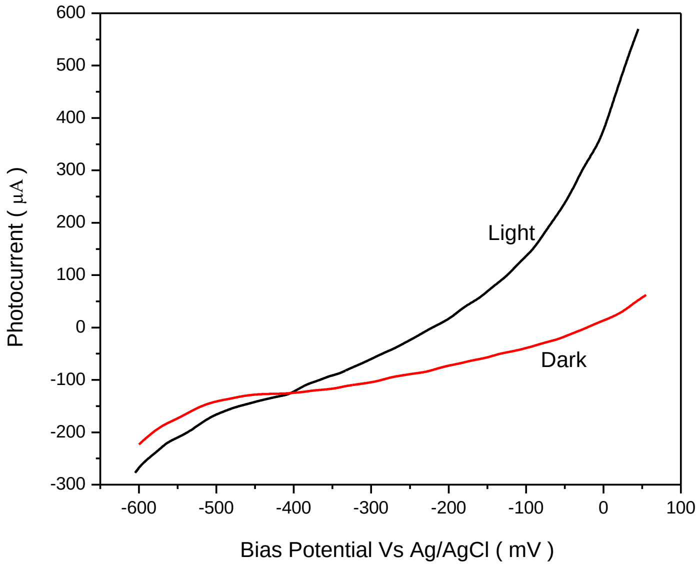

Fig.6: Dark and light current-voltage measurements of an n-Cu_2O/p-Cu_2O homojunction thin film, in a PEC containing 0.1 M sodium acetate solution

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cathodic potential is increased, p-type signal increases due to the front p-type film. This behavior wasfurther studied by the spectral response measurements with different bias conditions. Fig.7 shows the spectral response spectra of the n-p hormojunction having different bias conditions in the PEC containing 0.1 M sodium acetate. Although n-p homojunction produces n-type photocurrent in the entire spectral range atzero bias, poor photocurrent can be seen at short wavelength region. This can be easily understood because the existence of two junctions, namely the p-Cu_2O/electrolyte and the n-p homojunction. With the increase of cathodic biasp-Cu_2O/electrolyte junction produces p-type photocurrent in the entire spectral range. This behaviour indicates that the n-p hormojunction effectively generates both n- and p-type photocurrents in a PEC. n-type photocurrent generates by the n-p homojunction while p-type photocurrent produced by the electrolyte/p-Cu_2O interface as shown in energy band diagram of Fig. 8. Thereby the photocurrent of the device is n-type at zero bias and p-type at high cathodic bias. These results clearly show that the formation of n-p homojunction of Cu_2O. Solar cell fabrication using this homojunction with proper front contact is in progress.

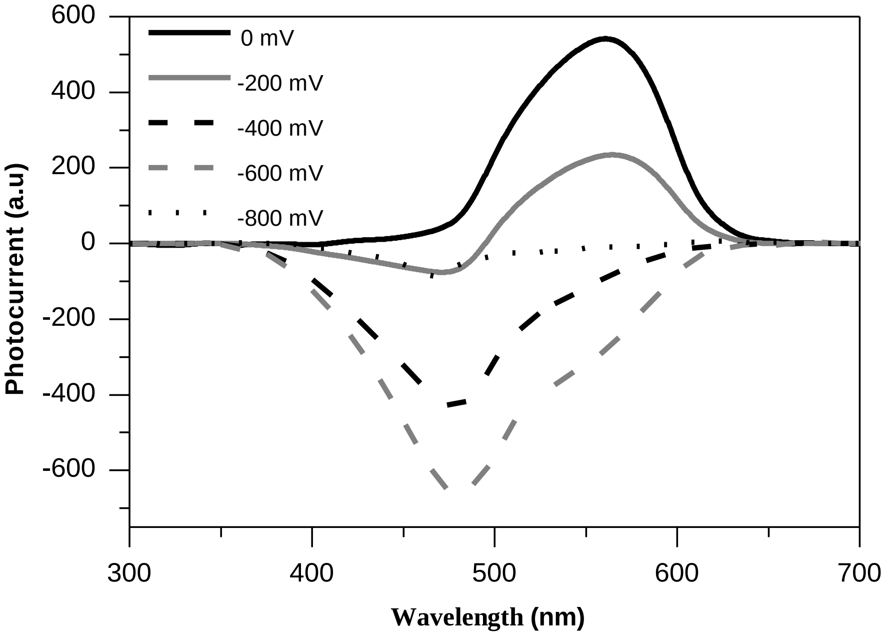

Fig.7: Spectral response measurements of an n-Cu_2O/p-Cu_2O homojunction thin film for different bias voltages, in a PEC containing 0.1 M sodium acetate solution.

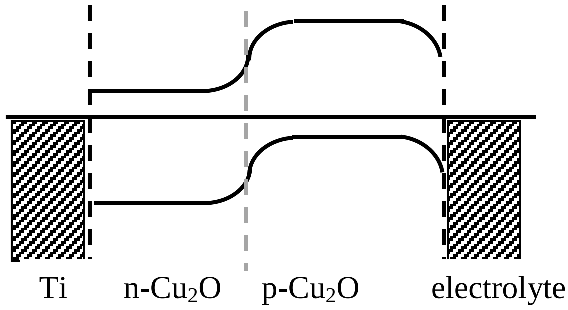

Fig. 8: Energy band diagram ofTi/n-Cu_2O/p-Cu_2O/electrolytesystem

Bulk structure of the n-p homojunction was studied using XRD measurements. Fig. 9 shows the XRD spectrum of the n-Cu_2O/p-Cu_2O homojunction fabricated on Ti substrate. It shows five peaks corresponding to the reflection from (110), (111), (200), (220) and (311) atomic planes of Cu_2O in addition to the Ti peaks. It is evident that there are no additional peaks corresponding to the impurity materials.

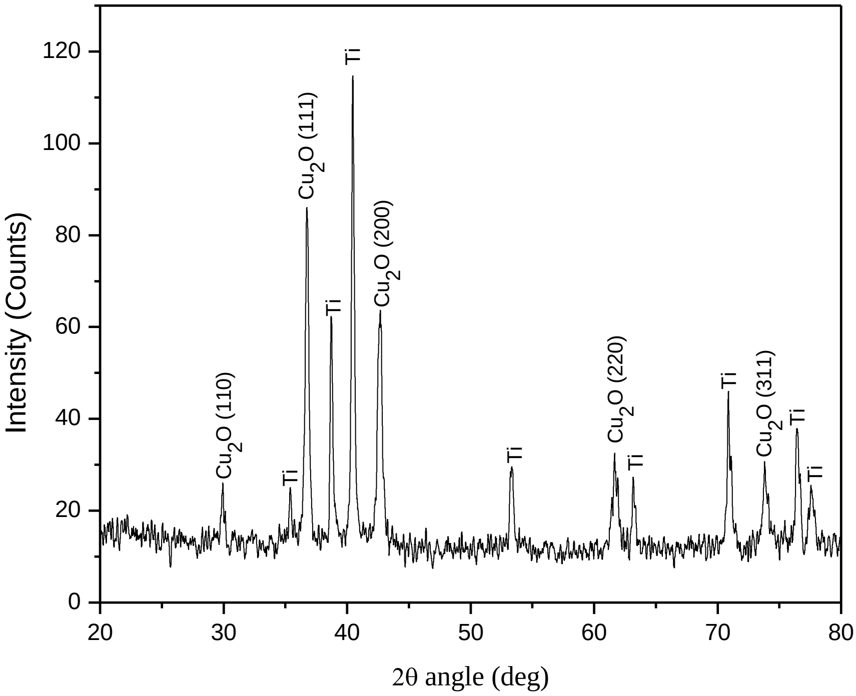

Fig.9: X-ray diffraction (XRD) spectrum for n-Cu_2O/p-Cu_2O homojunction thin film deposited on Ti substrate

4.0 CONCLUSION

The conductivity type of potentiostatically electrodepisited Cu_2O films strongly depends with the pH and cupric ion concentration of the acetate bath. Results revealed that improved n-Cu_2O can be elctrodeposited at pH 6.1 while improved p-Cu_2O can be elctrodeposited at low cupric ion concentration of 0.001 M. Furthermore, n- type conductivity can be improved by annealing the electrodeposited films at 100^oC for 24 hours in air.In conclusion, presentstudy reveals that p-Cu_2O can be electrodeposited on n-Cu_2O in acetate bathusing a very low cupric ion concentration and there by an efficient n-p homojuncton of Cu_2O can be fabricated suitable for applications in thin film solar cell devices.

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