The Effect of pH Solution on Electrodeposit-N-Cu_2O Thin Film

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***Abstract*—n-type semiconducting Cu_2O thin film was successfully prepared on FTO coated glass substrate using electrodeposition method. The effect of pH solution was studied in order to optimize the deposition parameters of n-Cu_2O. The solution was prepared using copper acetate and acid lactic. The pH solution was accurately adjusted using potassium hydroxide and varied from 3.5 until 6.5. The n-Cu_2O was successfully deposited at higher pH solution from 5.5 until 6.5. Moreover, it showed excellent structural characteristic and good morphology properties. The Cu_2O was adsorbed light at approximately 600 nm corresponding to the bandgap of 2.0 eV. The successful fabrication of n-Cu_2O was confirmed and the significant effect of pH solution was observed.**

***Index Terms*—Electrodeposition; n-Cu_2O; pH Solution.**

I. INTRODUCTION

Cu_2O is a naturally p-type semiconductor with the reported bandgap energy of 2.1 eV [1]. It has gained attention as a light-absorbing layer in oxide-based solar cells due to several significant advantages such as abundance materials with a theoretical conversion efficiency of 18 % [2].

The photovoltaic devices composed of cuprous oxide (Cu_2O) and zinc oxide (ZnO) materials have received broad attention as a candidate of next generation thin film solar cell due to several advantages such as these materials are abundance and non-toxic [3-4]. Moreover, the coefficient efficiency of Cu_2O is much lower than single-crystalline Si [5]. The Cu_2O absorbing layer has been prepared by several methods such as thermal oxidation [6], electrodeposition [3,4,7] and sputtering [8]. The highest conversion efficiency of Cu_2O-based heterojunction was at 5.38 % for the Cu_2O prepared by thermal oxidation with the combination of ZnO and Ga_2O_3 prepared by pulse-laser deposition method [9]. Compared to others, electrodeposition is a well-known deposition method which offers significant advantages (i) stable and repeatable, (ii) low-cost processing and (iii) possibility of large-scale deposition [10]. However, the conversion efficiency of Cu_2O-based heterojunction prepared only by electrodeposition was 1.28% for randomly oriented Cu_2O/ZnO heterojunction deposited on FTO glass substrate previously reported in 2007 by M. Izaki et. al. [7], which is twice than that prepared by sputtering method [8].

The best approaches to enhance the solar cell efficiency are to obtain the n-type semiconducting Cu_2O and the fabrication of pn homojunction of Cu_2O [11]. This is probably due to the large built-in- potential and lowest mismatch value. However, it is quite hard to obtain the n-type Cu_2O, due to the difficulties to optimize the amount of copper and oxygen vacancies in cuprous oxide; which are believed to be the cause of conductivity in the film. This problem could be solved by applying the electrodeposition method since it was found that the solution pH can control the conduction type of electrodeposit-Cu_2O [11-12]. Until to date, the reported work of n-Cu_2O is more focus on the construction of homojunction, there are lack data on parameter optimization and also the structural and morphological properties [11,13].

Here, the fabrication and investigation of n-type semiconducting-Cu_2O(n-Cu_2O) thin film on Fluorine-doped tin oxide (FTO) glass substrate using electrodeposition method. The electrodeposition method was selected due to the possibility to optimize the copper and oxygen vacancies in Cu_2O, which affect the Cu_2O polarity. An important parameter which is pH solution was investigated in order to optimize the deposition parameter of n-Cu_2O suitable for pn homojunction construction.

The structural, morphological and optical characteristics of electrochemical deposit n-Cu_2O was carried out using X-ray Diffraction (XRD), Field emission-scanning electron microscope (FE-SEM), Spectrophotometer (UV-Vis), respectively.

In this study, pH solution exhibited significant effect on n-Cu_2O thin film. This result will open new doors of developing homojunction thin film as well as the conversion efficiency increment.

II. EXPERIMENTAL

The The n-Cu_2O thin film was deposited on FTO glass substrate using electrodeposition method. Conventional electrochemical cell with simple three electrodes was used for the fabrication. The FTO glass substrate was cut approximately to 2.5 cm x 1.0 cm and the target deposition area was 1.0 cm^2. Prior to the deposition, the substrate was immersed into acetone and cleaned using ultrasonic cleaner. After that, the substrate was rinsed using distilled water. Finally, it was polarized in 1M NaOH at current density of +10mA/cm^2 about 60 sec. The Cu_2O film was deposited on FTO-coated glass substrate using an aqueous solution containing copper (II) acetate monohydrate and lactic acid by potentiostat electrolysis. The pH solution was adjusted by adding the Potassium Hydroxide (KOH). The pH solution was varied from 3.5 to 6.5 in order to investigate the effect of pH solution of n-Cu_2O thin film. The Cu_2O thin film was cathodically carried out at -0.1 V vs Ag/AgCl for approximately 30 minutes. The solution temperature was kept constant at 60 ^oC.

The investigation of the structural, morphological and optical characteristic of electrochemical deposit-n-Cu_2O thin films were carried out using X-Ray diffractometer (XRD), Field-Emission Scanning electron microscopy (FE-SEM), and Spectrophotometer (UV-Vis), respectively.

III. RESULTS AND DISCUSSION

A. Structural Properties

The structural properties of as-deposited cuprous oxide (Cu_2O) thin film were studied by using an X-ray diffractometer (XRD) with monochromated Cu Kα (1.54 Å) radiation. The scan range for 2θ is from 20 to 80 degrees. Figure 1 shows the XRD patterns of n-Cu_2O films deposited at pH solution 3.5, 4.5, 5.5 and 6.5. All n-Cu_2O thin films were prepared on FTO glass substrate.

At lower pH solution from 3.5 until 4.5, only one weak peak of Cu_2O was observed at 2ϴ value of 73.74^o, corresponding to the reflection from (311) of Cu_2O plane. Other than Cu_2O and the substrate peaks, the XRD spectrum also shows two high presence peaks of sub-oxide $Cu_{64}O$. It is known that the copper may form diverse oxides as it is a transitional metal. Oxides such as $Cu_{64}O$ may form due to the oxygen diffusing from the surface into the copper lattice. Several peaks corresponding to the Cu_2O were detected on XRD pattern of film prepared at higher pH solution of 5.5 to 6.5 (Figure 1(d)-(f)), in addition to those from substrate peaks. No other peaks such as metallic copper were detected on the XRD pattern. The peaks of Cu_2O are mainly involved orientation of (111) and (200). The preferred orientation of the sample prepared at pH solution 5.5 until 6.5 are (111)-Cu_2O (at 2ϴ=36.45^o), as reported previously for Cl-doped semiconducting Cu_2O [12]. The peak intensity of (111)-Cu_2O for all conditions (from 5.5 to 6.5) is almost consistent. From this result, it is believed that the film fabricated at pH solution between 5.5 and 6.5 are suitable for homojunction construction since (1x1) Cu_2O (111) [110] || (1x1) Cu_2O (111) [110], which theoretically exhibited lowest mismatch value. It can conclude that the structural of the film is significantly affected by the pH value during the deposition. Controlling the pH value can affect the different composition of cuprous oxide (Cu_2O). The Cu_2O is successfully obtained at higher pH solution of 5.5 until 6.5. From the previous reported study, the thin film prepared at higher pH solution around 6.0 shows lower resistivity related to the (111) orientation [11].

B. Morphological Properties

Figure 2 shows the Field Emission-scanning emission microscope (FE-SEM) images of the Cu2O thin films deposited at pH solution of 3.5 until 6.5. The solution temperature was kept constant at 60°C and the deposition time was 30 minutes.

The samples prepared at lower pH solution (Figure 2 (a)-(b)) show different morphology compared to those prepared at higher pH solution (Figure 2 (c)-(e)). The mixture shape of triangular and pyramidal of Cu2O was obviously seen for the thin film prepared at higher pH solution between 5.5 and 6.5, which is corresponding to the <111> facet of Cu2O. The shape of triangular and pyramidal is a typical morphology of Cu2O and this result is consistent with the previously reported for p-Cu2O [4]. However, the thin films prepared at lower pH solution were exhibited totally different morphology, which is believed originating from sub-oxide copper. This result is agreed with the structural properties.

C. Thin Film Composition

The composition of thin film was analyzed using Energy Dipersive X-Ray Spectroscopy(EDX). The sample prepared at pH solution of 6.0 was analyzed and the result shown in Figure 3. The EDX analysis revealed the presence of copper and oxygen from the FTO glass substrate. EDX spectrum of the film shows that, Copper (Cu) and Oxygen (O) incorporated into the film with the percentage of 56.09% (Cu) and 39.96% (O).

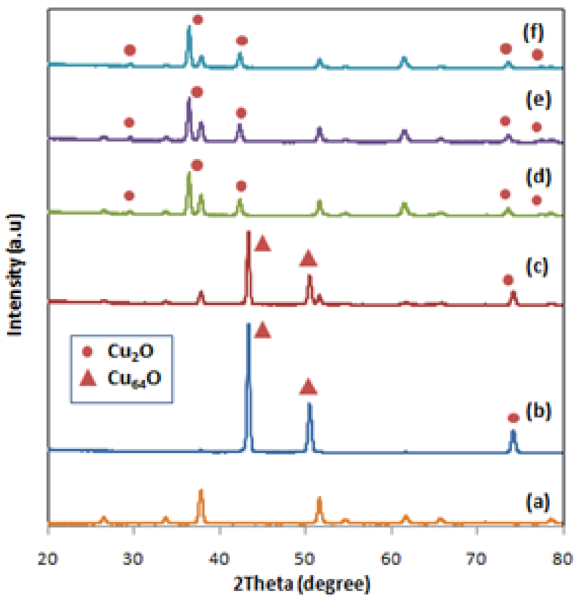

Figure 1: X-ray diffraction (XRD) patterns of (a) FTO substrate and Cu_2O thin film prepared at pH solution of (b) 3.5, (c) 4.5, (d) 5.5, (e) 6.0 (f) 6.5

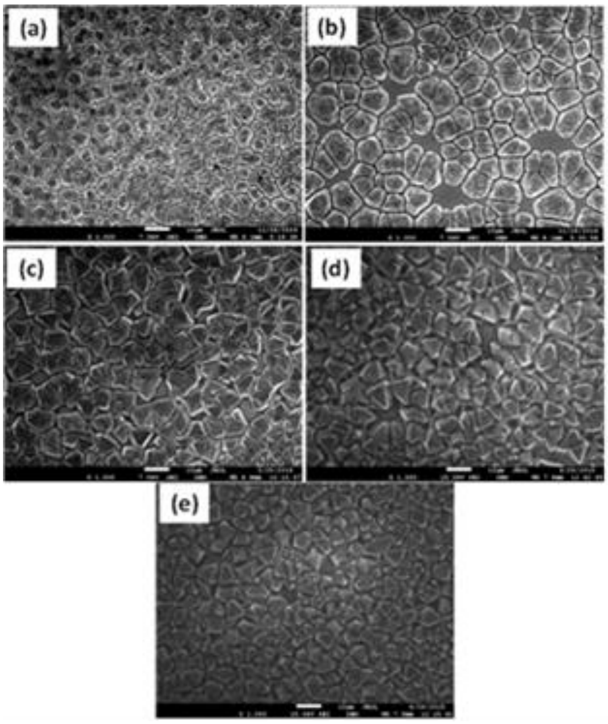

Figure 2: FE-SEM images of Cu_2O thin film prepared at pH solution of (a) 3.5, (b) 4.5, (c) 5.5, (d) 6.0 and (e) 6.5

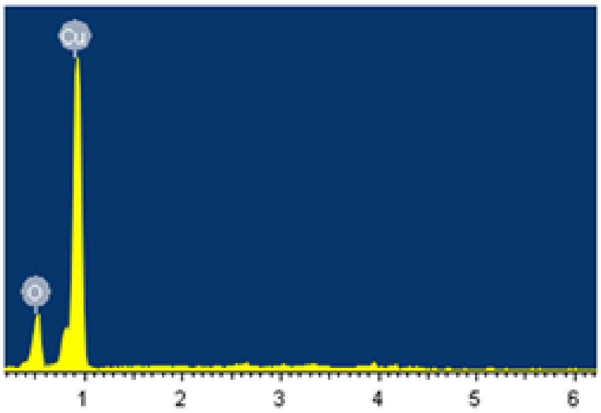

Figure 3: Energy Dipersive X-Ray Spectroscopy (EDX) pattern of Cu_2O thin film

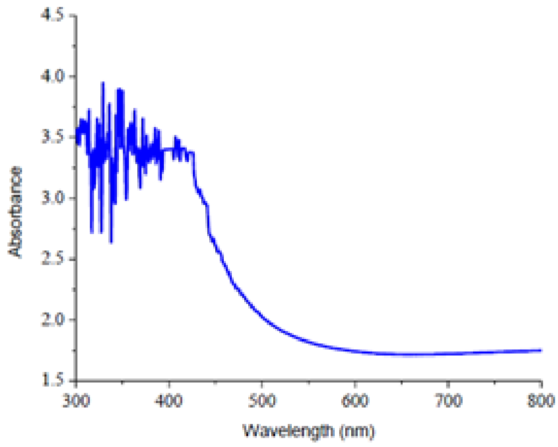

Figure 4: Absorption spectrum of n-Cu_2O thin film

D. Optical Properties

Figure 4 shows the UV-Vis spectrum of Cu2O thin film prepared at pH solution of 6.0. Cu2O thin film is strongly absorbing at wavelengths around 600 nm corresponding to the bandgap 2.0 eV of Cu2O. This result is consistent with the previously reported for p-Cu2O [4]. Although the polarization is different, the bandgap of n and p-Cu2O is remaining the same.

IV. Conclusion

Cu_2O-based heterojunction thin films have received broad attention as a candidate of next generation thin film solar cell alternative to silicon due to several advantages. pn homojunction is one of the best approaches to enhance the conversion efficiency. In this work, the investigation of pH solution was studied in order to optimize the deposition parameter of n-type Cu_2O thin film.

n-type semiconducting-Cu_2O thin films were successfully electrodeposited onto FTO glass substrates by the confirmation of XRD measurement, FE-SEM observation and EDX analysis. We have revealed the pH solution exhibited significant effect on electrodeposit-n-Cu_2O thin film. The n-Cu_2O was successfully fabricated at higher pH solution of 5.5 and 6.5 with (111)-preferred orientation. The triangular facet corresponding to the <111> plane of Cu_2O was observed for that prepared at pH solution temperature of 5.5 until 6.5. The structural and morphology properties of n-Cu_2O obtained are suitable for Cu_2O based homojunction. Although some improvement is needed, the result obtained in this study will open a new door for enhancement of conversion efficiency of Cu_2O-based thin film fabrication.

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