Effect of Mg Doping Concentration on Structural, Morphology, and Optical Properties of Electrodeposited Cu$_2$O Layer

N Nisha Razalli$^{1}$, M Zamzuri$^{2}$, M Mahyiddin$^{3}$, M Marina$^{4}$, A Rozie Nani$^{5}$ and M Izaki$^{6}$

1,2,4,5 Faculty of Mechanical Engineering Technology, Universiti Malaysia Perlis, Pauh Putra Main Campus, 02600, Arau, Perlis, Malaysia.
3 Faculty of Electronic Engineering Technology, Universiti Malaysia Perlis, Pauh Putra Main Campus, 02600, Arau, Perlis, Malaysia.
6 Department of Mechanical Eng., Toyohashi University of Technology, 1-1 Hibari Gaoka, Tempaku, Toyohashi, Aichi 441-8580, Japan

E-mail: mzamzuri@unimap.edu.my, nishanajjini@studentmail.unimap.edu.my

Abstract. The present work shows the effect of magnesium doping on structural, morphology and optical properties of Cu$_2$O layer prepared by electrodeposition method. The magnesium concentrations for doping on Cu$_2$O layers were 0.1 ~ 0.3 M of Mg(OH)$_2$. The structural, morphology, and optical properties of Cu$_2$O layer were characterized by using Field Emission Scanning Electron (FESEM), Ultraviolet-Visible Spectroscopy (UV-Vis), and X-ray Diffractometry (XRD) respectively. The variation of magnesium concentration shows significant impact and effect on the Cu$_2$O layer properties. The fabrication of doped Cu$_2$O layers reached up to 0.3 M dopant concentration, resulting in morphology changes. The grain size increase within among dopant concentration, however it become smaller and compact after doped with 0.3 M. In structural properties, XRD results show the peaks assigned for (111) of Cu$_2$O, (002) of CuO, and (200) of MgO, and the crystallite size for undoped until 0.2 M increased from 417.8 to 527.5 Å compatible with an observation by FESEM and optical absorption for 0.2 M.

1. Introduction
Cuprous oxide (Cu$_2$O) is one of p-type semiconductor with a direct band gap of 2.0 to 2.6 eV [1], that act as a light absorber in the solar cell. Over the year, Cu$_2$O has gained broad attention among researchers due to its good optical and electronic properties [2]. The advantages of Cu$_2$O in the optoelectronic application includes its direct-transition band structure that suitable for solar radiation absorption with the theoretical photovoltaic conversion efficiency of approximately 20% according to Shockley-Quieser Criteria (SQC) [3], low cost, nontoxicity, and excellent properties. However, since their electrical properties have a prescribed efficiency, they cannot be practically applied. The low record efficiency comes from numerous factor that remain poorly understood in Cu$_2$O, including the poor mobility of minority of carrier, un-optimized band structure, and high recombination [4]. The trap state that generated by inherent defect of Cu$_2$O that prevent diffusion of minority carrier [1]. Therefore, alternative method such as doping can prevent the creation of trap state which is expected to increase Cu$_2$O photoconductivity and solar efficiency.
Cu2O layers have been prepared by a variety of deposition methods such as nebulizer pyrolysis [5], thermal oxidize copper sheet [6], magnetron sputtering [7], spin coating [8], and electrodeposition method have recently been reported [9]. Electrodeposition is a common method used for the deposition of Cu2O layers on a substrate. It is a simple and reasonable cost of electrochemical technique that allows the broad area for thin film manufacturing [10].

On the other hand, the doping process has been used to control the properties of semiconductors in the most electronic device. The implementation of doping cuprous oxide with isovalent impurities of dopant in thin film solar cells increases the possibility to tune its energy band structure to suit the requirement of the optoelectronic application. In previous study, some material like Calcium (Ca) [11], lithium (Li) [12], gadolinium (Ga) [13], and magnesium (Mg) [14] are used as dopants in Cu2O nanoparticle. However, magnesium itself can greatly adjust the bandgap without changing the material structure, and compared with all other dopants, its band gap value can be increased to 3.50 eV to 4.50 eV doped to ZnO [15] and 2.20 eV to 2.4 eV doped to Cu2O [16]. Thus, this study is eventually intended to improve the photovoltaic efficiency performance by fabrication of Mg doped Cu2O via electrodeposition technique. The effect doping concentration on the surface modification on Cu2O layers is studied to improve the restricted light absorption spectrum.

2. Experimental section
Indium Tin Oxide (ITO) glass with dimension 2 cm of length x 1 cm of width x 0.75 mm of thickness was used as a substrate. Prior to electrodeposition process, ITO glass was separated into two areas which are deposited and non-deposited before immersed in acetone for about 2 minutes. Next, the glass substrate was rinsed with deionized water, then followed by drying with pressurized air.

2.1. Electrodeposition of undoped and Mg doped Cu2O layer
The electrodeposition of Cu2O layer was carried out in two electrodes, in which Pt plate and ITO substrate glass were used as the counter and working electrode with constant voltage of 1 V, where the current input was around 2 mA and deposition time was set up for 3 minutes. A platinum plate is used as an anode because it cannot be oxidized as a cathode. The electrolyte solution used for Cu2O layer deposition was prepared by dissolving 0.4 M of copper (II) acetate monohydrate (Cu(H2O)4CuO). 3.0 M of lactic acid (C3H6O3), and 3.7 M of potassium hydroxide, KOH into 500ml of deionized (DI) water at room temperature. The solution was adjusted until the pH becomes 12.5 with added KOH. Magnesium hydroxide (Mg(OH)2) was varied as 0.1 M, 0.2 M, and 0.3 M in the starting solution for the Mg doped Cu2O system. Furthermore, the Cu2O layers will be referred to as undoped, 0.1M, 0.2M, and 0.3M of molar concentration.

2.2. Characterization of analysis
The appearance of Cu2O on the ITO glass substrate undoped and doped with Mg was observed by optical microscopy (MOTICAM 1000 Optical Microscope) with 20x magnification. Then, morphology characterization was observed by Field emission scanning electron (FESEM Leo 1525-12-95), operated with 7kV of acceleration voltage and 50k and 70k of magnification. X-ray Diffractometer (XRD BRUKER D2 PHASER) was operated with a scan range of 20⁰ to 80⁰, 0.1s/step of scan rate, and 0.0002° of step size that linked with DIFFRAC.SUITE EVA Software was observed the structural characterization. The crystallite size (Å) can be calculated using the Debye-Scherrer. Next, the optical properties of films were observed by ultraviolet and visible absorption spectroscopy (PerkinELMER LAMBDA 950 Series) in the wavelength range of 200-800 µm referenced to the air.

3. Result and Discussion
3.1. The appearance of Mg doped Cu2O layers
The schematic illustration of Mg doped Cu2O on ITO substrate is shown in Figure 1. The Cu2O layer was deposited on ITO substrate with different concentrations of 0.1 M, 0.2 M, and 0.3 M Mg. Figure 2 shows the physical appearance of Cu2O layer before and after doping with different concentration of
Figure 1 Schematic illustration of cell configuration of Mg doped Cu$_2$O on ITO substrate glass.

Figure 2 The physical appearance of (a) ITO substrate glass, (b) undoped Cu$_2$O layer, (c) 0.1 M, (d) 0.2 M, and (e) 0.3 M of Mg doping concentration.

Figure 3 FESEM image of (a) the undoped Cu$_2$O layer, (b) 0.1 M, (c) the 0.2, and (d) 0.3 M of Mg doped Cu$_2$O layer.

Mg. The clear color of ITO substrate becomes the uniform color of light brown after deposited with undoped Cu$_2$O and Mg doped Cu$_2$O. No clear appearance changes of Cu$_2$O layers with the different in Mg doping concentrations.

3.2. FESEM analysis of surface morphology
Figure 3 shows the morphology of undoped and Mg doped Cu$_2$O layers with different dopant concentrations. The Cu$_2$O grains show a pyramid-like structure [4] with an apparent uniform and compact layers irrespective of the doping concentration. However, the grain size distribution has changed according to Mg doping concentrations. The grain size increased as dopant concentration...
increased from 0.1 M to 0.2 M, but decreased after doping with 0.3 M as demonstrated in (Figure 3 (b-d)). This is due to the stress existed in the grains that changed the structure of grains after Mg doping in Cu$_2$O layers [17].

3.3. Structural properties
X-ray diffraction (XRD) analysis was carried out to examine the crystal structure and orientation of undoped Cu$_2$O and Mg doped Cu$_2$O layers. Figure 4 (a) shows the XRD patterns for the electrodeposited Cu$_2$O layer with different concentrations of Mg doping varied from 0.1 ~ 0.3 M. The undoped Cu$_2$O layers revealed orientation which was indexed to (111) at 36.4° of diffraction peak. In addition, the other peaks were present including (200) reflection at 43.0° of diffraction peak for undoped Cu$_2$O layer. The Cu$_2$O orientation was corresponding to the cubic pattern (PDF 01-071-3645). While, the peak assigned for MgO layers could be seen after the electrodeposition in the concentration of 0.1 M, 0.2 M, and 0.3 M respectively. The peak of MgO was indexed to (200) at 42.5° of diffraction peak. Furthermore, the peak indexed to the plane (002) at diffraction peak of 35.5° assigned for CuO was also observed.

3.4. Crystallite size versus doping concentrations
The crystallite size was obtained from the analysis of the X-ray Diffractometer by using Scherrer’s equation [18].

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\text{Scherrer Formula } D = \frac{K\lambda}{\beta \cos \theta}
\]

Where -D is a Scherrer constant, -\lambda is a wavelength of XRD, -\beta is FWHM, and -\theta is peak position. The crystallites size for Cu$_2$O layers with different Mg doping concentrations are summarized in Figure 5. From Figure 5, it shows that the size of the crystallites increased from 417.8 Å to 527.5 Å as the doping concentration increase up to of 0.2 M. And then decrease to 472.3 Å for 0.3 M. The effect of the magnesium content seems especially visible in the Cu$_2$O layer doped with 0.2 M, where the crystallite size is the largest and compatible with the calculated grains size obtained by FESEM images.
Figure 5 Crystallite size versus concentration of Mg doping on Cu$_2$O layers.

Figure 6 Absorption spectrum of undoped and magnesium doped cuprous oxide thin film.

3.5. Optical properties
Figure 6 shows the absorption spectrum of Cu$_2$O layers doping with Mg at different concentrations. The absorption spectrum was measured in the range of 300 to 800 nm at room temperature. The result shows that higher absorption bands are obtained after doping with Mg irrespective of the doping concentration. The absorption edge at wavelength 500 nm, the highest absorption band can be obtained for 0.2 M Mg doped Cu$_2$O layer corresponding to the photon energy of 2.4 eV, and the profile and the peak photon energy changed depending on the Mg concentrations. The absorption profile mainly depends on certain factors, such as lattice strain, film thickness, insufficient oxygen, and particle size on the samples [19].
4. Conclusions
The Mg doped Cu$_2$O layer has been constructed by electrodeposition method of the p-Cu$_2$O layer on the ITO substrate with different Mg concentrations. The Cu$_2$O layer was prepared by electrodeposition in an alkaline aqueous solution containing copper (II) acetate and lactic acid. The structural result shows the undoped Cu$_2$O layer possess with (111) preferred orientation and the formation (002) of CuO, whilst the Mg doped Cu$_2$O layers shows MgO peak which corresponding to the plane (200). FESEM exhibited that the Cu$_2$O layers possess pyramid-like structure and polycrystalline nature. The increasing in the Mg concentration resulted in the change of grain size of the Cu$_2$O structure due to stress existed in the crystals after doping. Although further enhancements are required, these outcomes demonstrate the importance of the crystalline structure of the Mg doped Cu$_2$O layers to improve the performance of the photovoltaic device.

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