Photocurrent Enhancement of P-Cu_2O Thin Film Achieved by Thermal Annealing

Yu-Kuei Hsu and Hung-Hsun Lin

***Abstract*—The effects of annealing on the photocurrent enhancement of *p*-Cu_2O thin film were systematically investigated in this report. The thermal annealing process under the N_2 atmospheres obviously improved the crystallization of Cu_2O and release the compressed stress resulting from deposition of the film according to the results of XRD and Raman measurements. Furthermore, IPCE measurement was utilized to evaluate the bandgap of 2.1 eV in Cu_2O thin film. Significantly, the annealed Cu_2O thin film exhibited the six times enhancement of photocurrent in comparison with as-grown sample.**

***Index Terms*—Cu_2O, electrodeposition, photoelectrochemical.**

I. Introduction

Among alternative energy production methods, the solar-powered splitting of water into hydrogen and oxygen is a favorable means of converting solar energy into a "solar fuel", since both water and sunlight are hugely abundant [1]-[2]. The generation of hydrogen by photoelectrochemical (PEC) water decomposition under solar illumination is much simpler and more environmentally friendly than the catalytic reforming of hydrocarbon fuels [3]-[4]. Typically, solar conversion efficiency and the stability of PEC water decomposition are determined by the properties of the semiconductor materials that are used as photoelectrodes. Up to date, the *n*-type semiconductors are widely being developed for use in photoanodes, such as TiO_2, GaN and ZnO, but the photo-assisted etching reaction of *n*-type materials associated with the photo-generated hole is unavoidable when PEC water decomposition takes place. To eschew photo-etching problem, the utilization of *p*-type semiconductors is required, because the reductive electrons instead of the oxidative holes drive the water splitting reaction. Among the various *p*-type materials, binary copper semiconductor, especially copper oxide in the form of cuprous oxide (Cu_2O) or cupric oxide (CuO), are attractive because they are *p*-type photoactive materials, copper is abundant and the materials can be processed by industrially proven, low-cost methods [5]-[6]. Moreover, Cu_2O and CuO have relative low direct band gap of 2.1 and 1.3 eV, respectively, which make them a suitable candidate for light-harvesting devices. Over the past decade, the electrodeposition technique can offer reliable route to synthesize *p*-Cu_2O thin film. However, this as-grown thin film at the low temperature may have poor crystal quality. In order to improve the crystalline Cu_2O, the post-annealed treatment is necessary. But, the studies on the effect of thermal treatment for PEC application are relatively rare. In this report, different treatment under the various atmospheres.

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II. Experimental

In a typical electrodeposition process, a piece of Pt foil and a standard silver/silver chloride electrode (Ag/AgCl) were used as the counter and reference electrodes, respectively. Fluorine-tin oxide (FTO)-coated glass was used as a substrate and working electrode. FTO-coated glass was cleaned using acetone and rinsed with deionized water before use. All of the reagents are of analytical grade and used without further purification. Aqueous 4 M $CuSO_4$ and 0.3 M lactic acid were used as electrolytes. The NaOH was also added to adjust the pH value between 9 and 11. Electrodeposition was carried out using an electrochemical analytical instrument (CHI 627D). The applied potential was operated at various potential versus Ag/AgCl for 30 min. and the solution temperature was maintained at 60 ^{o}C. Finally, all of the samples were annealed at the temperatures of 300 ^{o}C and 500 ^{o}C for 1 h in nitrogen atmospheres.

The morphology of hybrid copper oxide arrays were examined by scanning electron microscopy (SEM, JEM-4000EX), and the structure of the samples was analyzed using X-ray diffractometer (XRD, Bruker D8 Advance diffractometer) with Cu K_α radiation (λ=0.1506 nm). Raman spectra were measured using a LabRAM HR 550 system equipped with a HeNe laser (632.8 nm, 5 mW) and a 100x objective. The photo-electronchemical behavior of the electrodes was measured in 0.5 M Na_2SO_4 solution. A 150 W Xe lamp light source with an AM 1.5 filter was used, and the intensity of the illumination at the sample position was determined to be 100 mWcm^{-2}. In addition, a 150 W Xe lamp equipped a monochromator was used as the excitation light source to obtain monochromatic light for incident photon-to-electron conversion efficiency measurement. The incident light was irradiated onto Cu_2O thin film electrodes from the front face through the quartz window and the electrolyte unless noted otherwise.

III. Results and Discusion

The morphologies of as-grown thim film and annealed sampled were analyzed by SEM, as shown in Fig. 1. The as-grown sample shows a clear pyramid-like morphology,

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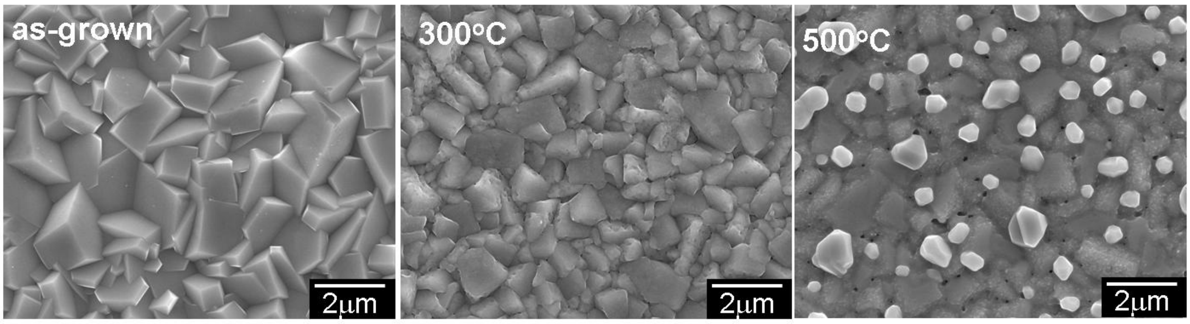

Fig. 1. SEM results of as-grown thin film and annealed sample at annealing temperature of 300°C and 500°C.

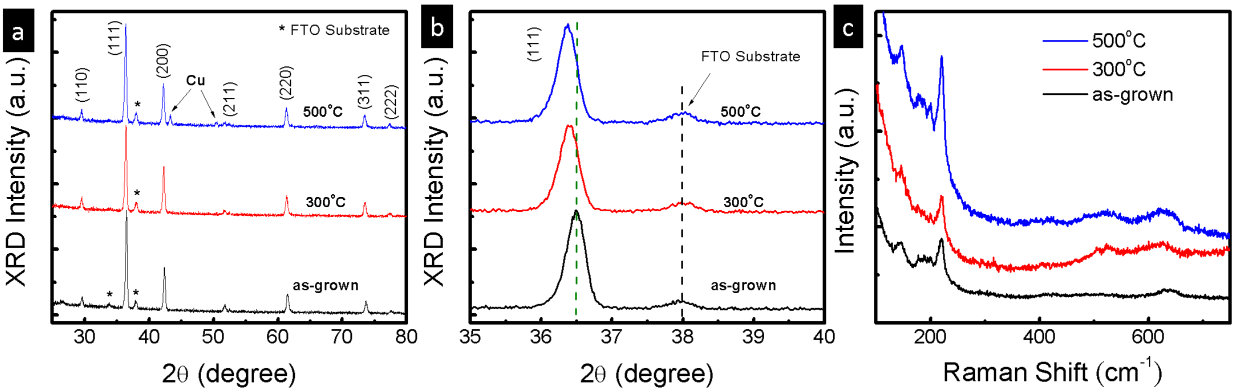

Fig. 2 (a) X-ray diffraction patterns of as-grown Cu_2O thin film and annealed samples. (b) Relative change in (111) peaks from Cu_2O thin film. (c) Raman spectrum of as-grown Cu_2O thin film and thermal treated samples with the annealing temperature of 300 °C and 500 °C.

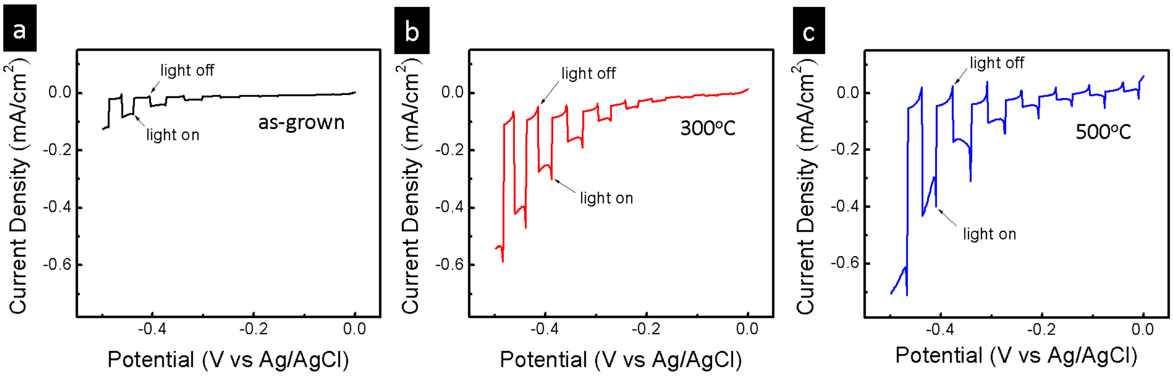

Fig. 3. Photocurrent-voltage responses of (a) as-grown Cu_2O thin film, and annealed Cu_2O at the temperature of (b) 300 °C and (c) 500 °C.

which composes of tilted {100} faces and exhibits 3-fold rotational axes at the center of triangular faces and 3-fold axes at the apexes as shown in Fig. 1 (a) . This morphology can also agree with the cubic structure of Cu_2O film later. When the film annealed at 300 °C (Fig. 1 (b)), the individual pyramid-like grains became much coarse and considerably porous as compared to those in the as-deposited films. As increasing the annealing temperature to 500°C, the pyramid-like grains were notably absent, inferring possible nucleation and grain growth was occurring during annealing (Fig. 1 (c)). In addition, the sub-micro particles appeared on the top of film, which was deduced form the reduction of Cu_2O to metallic Cu.

The crystal phases of the samples under different annealing temperatures were determined using powder XRD, as shown in Fig. 2 (a) . The XRD pattern of as-grown sample is also displayed for comparison. First, the diffraction peaks from as-grown sample are identified as cubic-phase (JCPDS card No. 78-2076) of Cu_2O, beside the peaks of FTO substrate. As the annealing temperature increase, the main peak of (111) obviously shift to low angle (Fig. 2 (b)), which indicates the release of compressed stress during the growth of thin film. Therefore, this annealing process may benefit the reconstruction of Cu_2O thin film, and further improve the crystal quality of film. As regards the diffraction pattern in the annealing temperature of 500 °C, two diffraction peaks originated from metallic copper were found. This phenomenon could be ascribed to the process of deoxidization. Although the annealing process at 500 °C would reduce few Cu_2O to Cu, the most of the Cu_2O film could be significantly improved.

The structural formation of the Cu_2O thin film and the effect of thermal treatment were also studied by Raman scattering. Fig. 2 (c) shows the Raman spectrum of the as-grown Cu_2O film and annealed samples. The Raman spectrums of all samples show the characteristic phonon frequencies of the crystalline Cu_2O. The strong peak at 218 cm^{-1} originated from the second-order Raman-allowed mode of the Cu_2O crystals. The peak at 148 cm^{-1} may be attributed to Raman scattering from phonons of symmetry Γ^{-}_{15}. In addition, the weak peaks at 308 and 515 cm^{-1} correspond to the second-order overtone mode $2\Gamma^{(1)}_{15}$ – and the Raman-allowed mode, respectively. The peak at 416 cm^{-1} is assigned to four-phonon mode $3\Gamma^{-}_{12} + \Gamma^{-}_{25}$. The peak at 635 cm^{-1} is attributed to the infrared-allowed mode.[7] The characteristic peaks of CuO under the same experimental conditions at 298, 330 and 602 cm^{-1} could not be detected. It indicates that the annealing process does not oxidize the Cu_2O film, but the crystalline quality of the film could be improved according to the enhancement of the peak at 218 cm^{-1}. Also, this finding is consistent with the results of XRD.

To investigate the characteristic of photocurrent response in Cu_2O thin film under thermal annealing treatment, a three-electrode photo-electrochemical cell was adopted for analysis. Herein, the chopped light was periodically illuminated on the sample at a rate of 2 s exposure following every 2 s unilluminated, and the current was recorded while the voltage was changed from 0 to -0.5 V. For all samples, a clear increase in the magnitude of the cathodic photocurrent was seen under light exposure, as shown in Fig. 3. These photo-induced cathodic currents result from the reduction of proton involving the photo-generation of electrons, revealing the *p*-type nature of Cu_2O thin film. Obviously, the photocurrents of annealed samples display the increase of photocurrent at the potential of -0.5 V vs Ag/AgCl. In comparison with as-grown Cu_2O film, the annealed sample at temperature of 500 °C exhibits approximately six times enhancement. The factor could be ascribed to the improvement of crystal quality and release of compressed stress. Furthermore, the photocurrent action spectra (Fig. 4) plot the incident photon-to-electron conversion efficiency (IPCE) as a function of excitation wavelength at a potential of -0.2 V. Significantly, the photoresponse of Cu_2O thin film is further extended into the red region at a wavelength of 620 nm (2.1 eV), originated from Cu_2O. After annealing treatment at the temperature of 500 °C, the conversion efficiency would be increased from 2 % to 9 % at the wavelength of 550 nm. This specific annealing process could be able to benefit the Cu_2O based light-harvesting device.

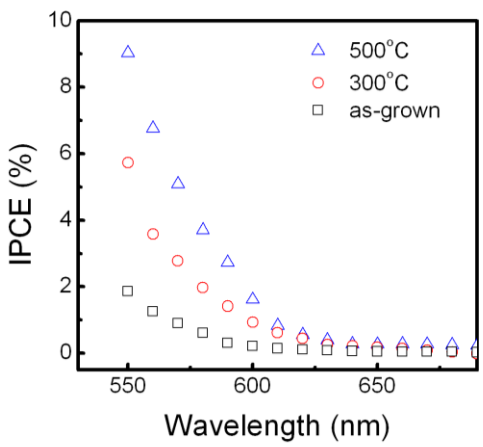

Fig. 4. IPCE of as-grown and annealed Cu_2O thin film.

IV. Conclusion

In summary, the effects of various annealing temperatures on the electrodeposited p-Cu_2O thin film were carefully carried out in nitrogen atmospheres. From XRD measurements, the cubic phase of Cu_2O was confirmed, and the release of compressed stress was observed according to the shift of (111) diffraction peak after annealing process. In addition, the thermal treatment also improved the crystalline quality of Cu_2O thin film by the observation of Raman results. From photoelectrochemical analysis, the photo-induced cathodic current was demonstrated the *p*-type nature of Cu_2O film. The bandgap of 2 eV in Cu_2O was evaluated by the results of IPCE. Significantly, the annealing sample exhibited six times enhancement of photocurrent in comparison with as-grown Cu_2O. Hence, the findings in this report could benefit the fabrication of low-cost photovoltaic materials for the application of solar cells.

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