

Cuprous oxide (Cu₂O) thin films for photoelectrochemical cell.

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Introduction

Cuprous oxide (Cu₂O) that is a non-toxic material is potentially attractive as an active electrode for PEC solar cell. Cuprous oxide thin films have been prepared by various techniques like thermal oxidation, chemical vapor deposition, anodic oxidation, reactive sputtering, pulse laser deposition, electrodeposition, plasma oxidation, etc (1-7). Cathodic electrodeposition is a good method to control easily the particle size and the film thickness (8). Cathodic electrodeposition takes place by the generation of OH⁻ and then neutralization of cationic species on the electrode surface. The deposition rate and the film thickness are usually 10⁻³-1 μm/min and 10⁻³-10 μm, respectively. Cuprous oxide is a semiconductor having the band gap of about 2.1eV so it can absorb the visible lights to make electivity. The p-type Cu₂O thin films were potentiostatically electrodeposited on ITO substrates. Depending on the voltage, Cu metal and/or Cu₂O oxide were detected on the as-deposited film by XRD. The Cu₂O particle size and the thickness are dependant on the deposition time, voltage, and the methods, normal or pulse. Normal cathodic electrodeposition was done at the same voltage. But in the pulse method, the voltage was changed from -3.0eV(0.1sec) to -0.5 eV (5sec) and then the cycle was repeated during the deposition. Cu₂O solution of 0.05mol (pH=4.3) was used for the Cu₂O electrodeposition. The as-deposited films were calcined at 300°C for 1 hr to oxidize Cu metal into the Cu₂O. The photocurrent was measured at the bias voltage of 0.6eV and the light quantity of 100mW/cm². The thickness of cuprous oxide films was measured using SEM.

Results and Discussion

Photocurrent on an oxide film would be dependant on the particle size and the film thickness. The film thickness should be optimized for the high photo efficiency in the point of view of maximum light absorption and minimum distance that an excited electron should transfer to avoid the electron-hole recombination in a PEC cell. Figure 1 showed different photocurrent on the cuprous oxide films depending on the deposition

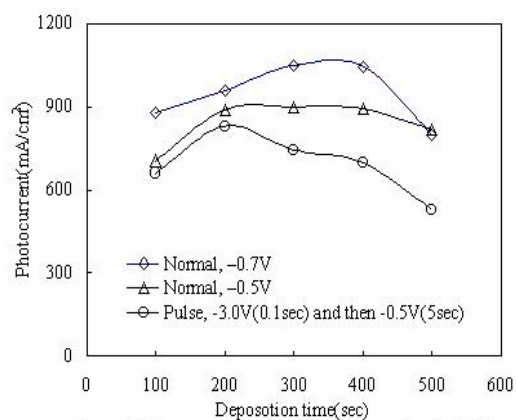


Figure 1. Photocurrent vs. deposition time on the Cu₂O thin film at light quantity of 100mW/cm².

voltage and the methods. The cuprous oxide deposited at -0.7eV by normal method indicates higher photocurrent than those deposited at -0.5 and by pulse method as shown in the figure 1. The particle size of cuprous oxide deposited at -0.7eV was bigger than those deposited at -0.5eV and by pulse method. It means that the recombination reaction could be easily happened in the small particles of Cu_2O because of the grain boundary increased. The deposition rate was slower in the normal method than in the pulse method. Therefore, the maximum point of photocurrent appeared at the different duration of deposition as shown in the figure 1.

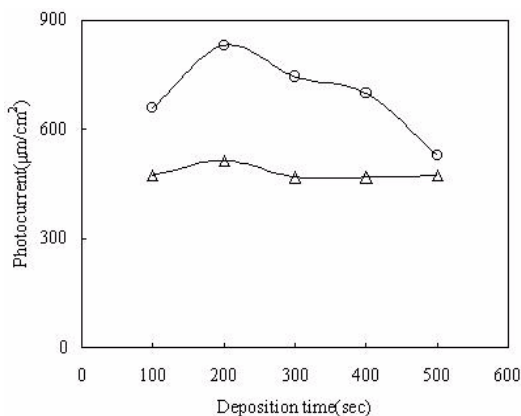


Figure 2. Photocurrent on Cu_2O film calcined for different duration

—○— Pulse, 300°C, 1hr calcine —△— Pulse, 300°C, 0.5hr calcine

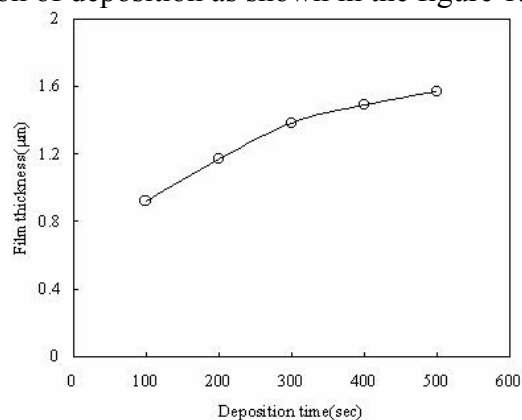


Figure 3. Film thickness of Cu_2O depending on deposition time

Figure 2 indicates the effect of calcination period on the photocurrent of cuprous oxide film deposited by pulse method. The cuprous oxide calcined at 300°C for 1hr shows higher photocurrent than that calcined at 300°C for 0.5hr. It means that the calcination for 30min was not enough to oxidize Cu metal into the Cu_2O and it was confirmed by XRD. According to the Pourbaix diagram of copper (8), the nucleation of Cu metal would be took place in the pulse of $-3.0\text{eV}(-0.1\text{sec})$ and then the metal particle grown at the $-0.5\text{eV}(5\text{sec})$. On the other hand, the difference of the photocurrent on the cuprous oxide film deposited by normal method is not high depending on the calcination period. Figure 3 shows the film thickness deposited by pulse method depending on the deposition time. The maximum photocurrent was shown on the film thickness of about $1.2\ \mu\text{m}$.

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