

NEW APPROACH FOR GENERATING $\text{Cu}_2\text{O}/\text{TiO}_2$ COMPOSITE FILMS FOR SOLAR CELL APPLICATIONS

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Abstract

In this paper, Cu_2O was studied as a photon absorber for solar cell applications. Cu_2O was deposited on a TiO_2 film using the electrochemical deposition (ECD) method. Based on the physical appearance of the samples, the particles of Cu_2O seemed to penetrate the TiO_2 film and were primarily deposited near the TiO_2 /substrate interface rather than on the TiO_2 film surface. This method could be one way to generate a p-n bulk-heterojunction interface. The film was confirmed to be a $\text{Cu}_2\text{O}/\text{TiO}_2$ composite via X-ray diffraction measurements. The top electrode was formed by evaporating indium for I-V characterization, and the fabricated cell showed photovoltaic properties.

Keywords: composite materials, electrodeposition, solar energy materials, thin films.

Introduction

TiO₂ is an n-type semiconductor with a wide band-gap energy of 3.2 eV and is known for having photo-catalytic effects [1]. Grätzel et al. developed a type of cell called a dye-sensitized solar cell (DSSC), or a Grätzel cell, and its efficiency can be improved by 11% with the use of ruthenium dye [2]. However, the Grätzel cell has problems with dye desorption, leakage, packaging and long-term stability. Many attempts have been made to improve the cells. One alternative solution is to convert it to a solid-state cell by using a p-type semiconductor as a hole conductor instead of a liquid electrolyte. Recently, many p-type semiconducting materials have been used in an attempt to convert cells to solid-state DSSCs, including Spiro-OMeTAD [3] and copper (I) iodide (CuI) [4-5]. However, contact between the dye monolayer and the p-type material is crucial in solid-state DSSCs. Therefore, previous attempts to resolve these problems have failed because only incomplete filling of the TiO₂ pores with a p-type material was achieved, especially when thicker films were used.

One way to overcome the problems with solid-state DSSCs is to use ETA (extremely thin absorber) solar cells or quantum dot (QD) sensitized solar cells, which are conceptually similar to solid-state DSSCs [6-9]. In those solar cells, a small band -gap p-type semiconductor, such as CuInS₂, CdTe and SnS replaces the molecular dye in the DSSC and works as a photon absorber in the cells [10-12]. The semiconductor typically covers the n-type semiconductor film, which is usually TiO₂. The structure of the ETA and QD solar cells has the advantage of enhanced light harvesting due to surface enlargement and multiple scattering [7-8]. The TiO₂/CdTe cells fabricated by Ernst et al. [10] exhibited an open-circuit voltage of 0.67V and a short-circuit current of 8.9mA cm⁻² under 100 mW cm⁻² of simulated sunlight. Nanu et al. [11] generated TiO₂/CuInS₂ solar cells using an atomic layer chemical vapor deposition method (ALCVD) with 4% solar energy efficiency.

Following these previous studies, we considered the use of cuprous oxide (Cu₂O) as a p-type solar cell material to be deposited on TiO₂ for solar cell applications. In this study, Cu₂O was used as a photon absorber. Cu₂O, with a direct band-gap of 2.1 eV, is regarded as a suitable material for high-efficiency solar cells [13-14]. McFarland et al. created a Cu₂O/TiO₂ heterojunction thin film and observed a photoresponse in a photoelectrochemical cell [15]. Li et al. prepared core shell Cu₂O/TiO₂ solar cell with an efficiency ~0.01%

[16]. The combination of Cu_2O and TiO_2 could contribute to efficient photoelectric conversion. In this research, $\text{Cu}_2\text{O}/\text{TiO}_2$ composite thin films were generated through a combination of electrochemical deposition (ECD) and squeegee methods, and a cell was fabricated by forming metal electrodes on the film. Through ECD, we observed that the particles of Cu_2O penetrated the nanoporous layer of the TiO_2 . The structural and optical properties of the films were also characterized, and the photoresponse of the cell was measured.

Experimental Procedures

TiO_2 films with a thickness of approximately 16 μm were prepared by the squeegee method using a 0.8 g/mL paste of TiO_2 powder (P25, Aerosol Japan) with 0.5 mL of acetyl acetone. The paste was mixed and blended with 0.4 g of polyethylene glycol and 2.5 mL of triton X for about 5 min. Then, the TiO_2 films were heated and annealed at 100°C and 400°C for 30 min in air. The substrate used was F-doped SnO_2 (FTO) coated glass. The deposition of Cu_2O on the TiO_2/FTO substrate by ECD was accomplished using an aqueous solution containing 0.5 mol/L copper (II) sulfate and 6 mL of lactic acid in 20mL of pure water. The solution pH was adjusted to 12.5 with KOH. Galvanostatic electrochemical deposition on the TiO_2/FTO substrate was performed at a current density of approximately $-1 \text{ mA}/\text{cm}^2$, and the deposition time was 10 min unless otherwise stated.

Results and Discussion

The physical morphologies of the films are shown in Figures 1 (a), (b) and (c). After the Cu_2O was deposited, the top surface remained white, while the bottom side (the substrate side) turned orange (the color of Cu_2O). Thus, the Cu_2O seemed to penetrate the TiO_2 film and was primarily deposited near the TiO_2/FTO interface rather than on the TiO_2 film surface. This result likely occurred because the Cu_2O gradually filled the porous matrix of TiO_2 from the bottom, as shown in Figure 1 (d). When Cu_2O was deposited, it is likely that the deposition solution easily penetrated the TiO_2 film. For Cu_2O to deposit on the top surface of the TiO_2 film, the electric current needed to flow through the TiO_2 matrix. However, the TiO_2 particles composing the matrix are resistive. Therefore, it is possible that the current preferentially flowed from the

film/substrate interface into the deposition solution. Thus Cu_2O was preferentially deposited near the interface rather than on the top surface.

Figure 2 shows X-ray diffraction patterns for the Cu_2O , TiO_2 and $\text{Cu}_2\text{O}/\text{TiO}_2$ composite films. All of the peaks observed for TiO_2 can be attributed to the TiO_2 anatase structure, and the peaks observed for Cu_2O can be attributed to the Cu_2O cubic structure. For the composite film, in addition to the TiO_2 peaks, Cu_2O peaks were also observed.

Figure 3 shows optical transmission spectra for the TiO_2 , Cu_2O , and $\text{Cu}_2\text{O}/\text{TiO}_2$ composite films. The Cu_2O film has an absorption edge around 570 nm, which corresponds to its band gap of 2.1 eV. The TiO_2 film was porous. Thus, the transmission was low in the visible range due to scattering. The absorption edge was observed near 400 nm. For the composite films, the transmission was minimal for wavelengths shorter than 520 nm due to absorption by the Cu_2O .

For the I-V characterization, indium was evaporated as shown in Figure 4 (a). Figure 4 (b) shows the photovoltaic behavior of the $\text{Cu}_2\text{O}/\text{TiO}_2$ composite films measured during illumination through the FTO glass substrate. Three samples with different Cu_2O deposition times were prepared and measured. The AM1.5 light intensity was maintained at 100 mW/cm^2 for all of the measurements. For the 10 min deposition sample, the short-circuit current was 0.0031 mA/cm^2 , the open-circuit voltage was 0.47 V, and the efficiency was $5 \times 10^{-4} \%$. Thus, a rectifying p-n junction was formed, with the front surface side acting as an n-type semiconductor and the film/substrate interface side acting as a p-type semiconductor. This arrangement likely occurred because the surface side was primarily comprised of TiO_2 and the interface side was primarily comprised of Cu_2O , as shown in Figure 2.

A solar cell based on a mixture of n-type and p-type semiconductors is commonly called a blend solar cell or a bulk-heterojunction solar cell. In almost all previous studies on bulk-heterojunction solar cells, the photovoltaic blend film consisted of two organic semiconductors or one organic and one inorganic semiconductor. We have demonstrated that the $\text{Cu}_2\text{O}/\text{TiO}_2$ composite film shows photovoltaic behavior, as shown in Figure 4 (c). Therefore, we can regard our composite film as an inorganic-inorganic bulk-heterojunction thin film.

Conclusions

Cu₂O films were deposited by ECD on TiO₂ films prepared by the squeegee method, and a cell was generated by evaporating In on the film. During I-V characterization, the cell showed electrical rectification and photovoltaic effects. Even though the overall performance of the cell has not yet been optimized, we have demonstrated that an inorganic bulk heterojunction solar cell can be created using a simple approach based on the ECD and squeegee methods.

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Figure 1: (a) Physical appearance of the TiO_2 film, (b) and (c) images of deposited Cu_2O on TiO_2 from the top and bottom sides view, respectively and (d) model of the $\text{Cu}_2\text{O}/\text{TiO}_2$ film structure.

Figure 2: X-ray diffraction patterns of (a) Cu_2O , (b) TiO_2 and (c) $\text{Cu}_2\text{O}/\text{TiO}_2$ composite films.

Figure 3: Transmission spectra for (a) Cu_2O (b) TiO_2 and (c) the $\text{Cu}_2\text{O}/\text{TiO}_2$ composite films.

Figure 4: (a) Position of the electrodes for the I-V measurement, (b) I-V curves for $\text{Cu}_2\text{O}/\text{TiO}_2$ composite films with different Cu_2O deposition times, (c) photo-response behavior from I-V characterization of the $\text{Cu}_2\text{O}/\text{TiO}_2$ composite films under an illumination of $100\text{mW}/\text{cm}^2$.

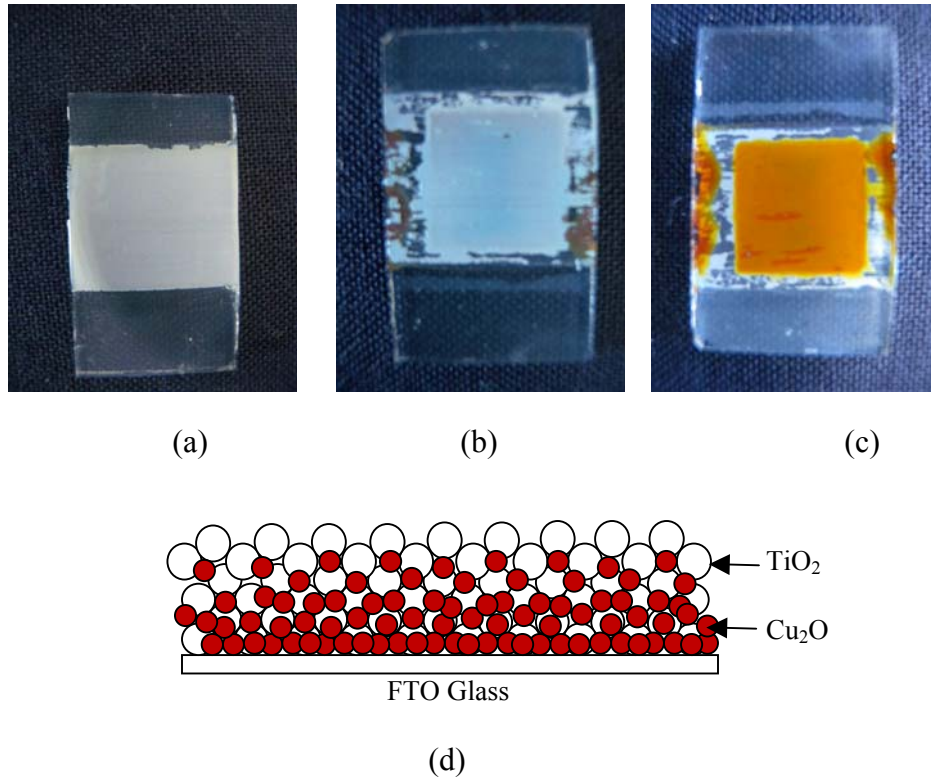


Figure 1

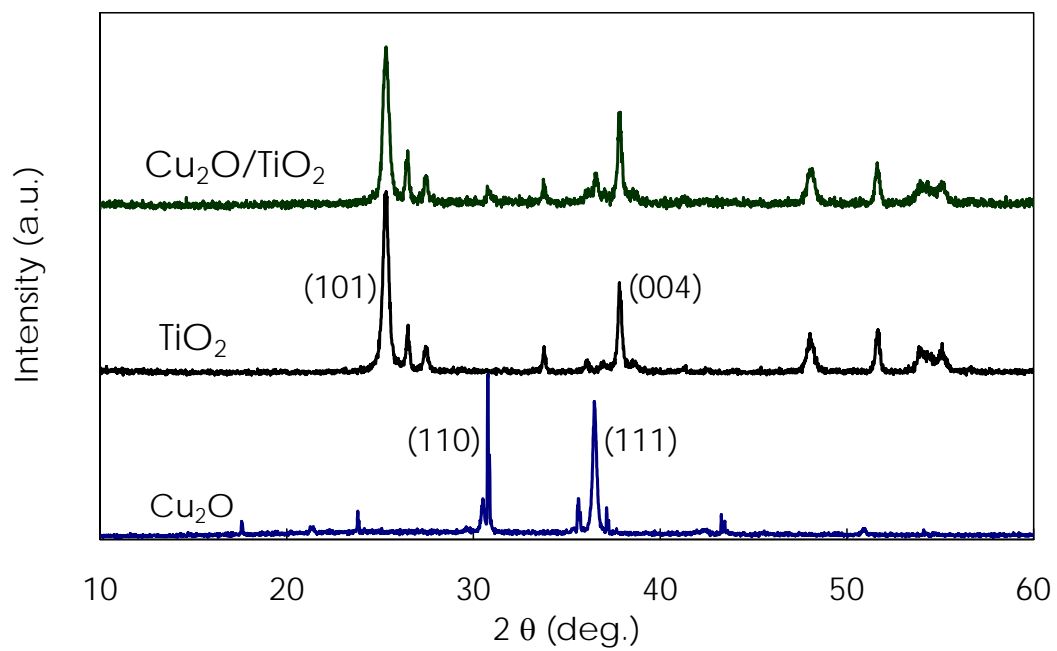


Figure 2

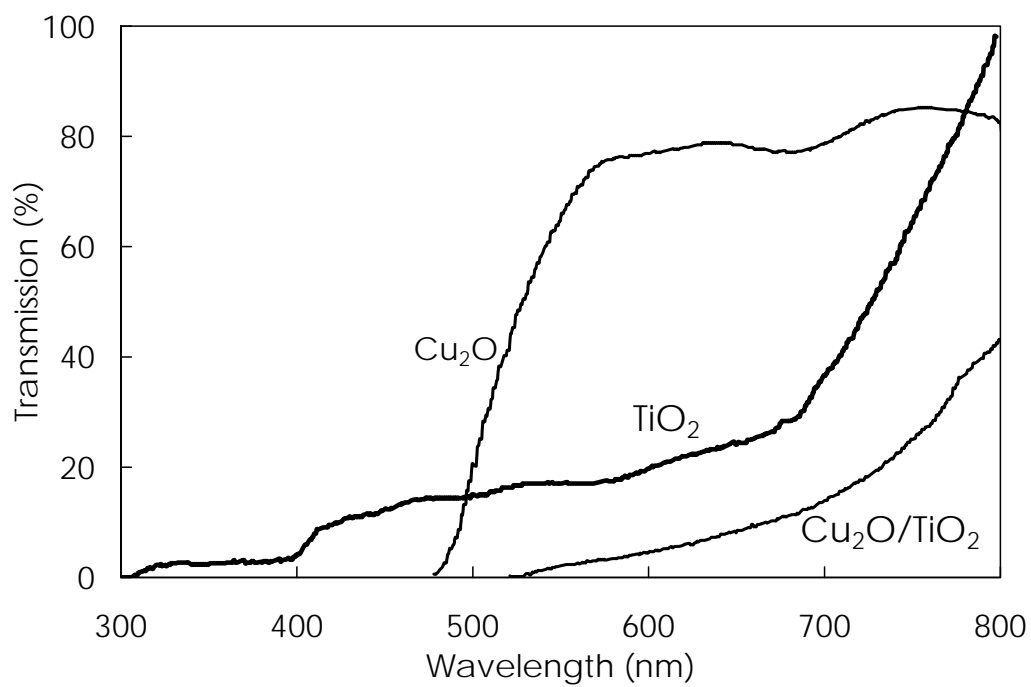
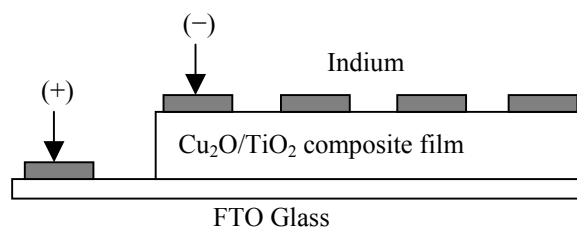
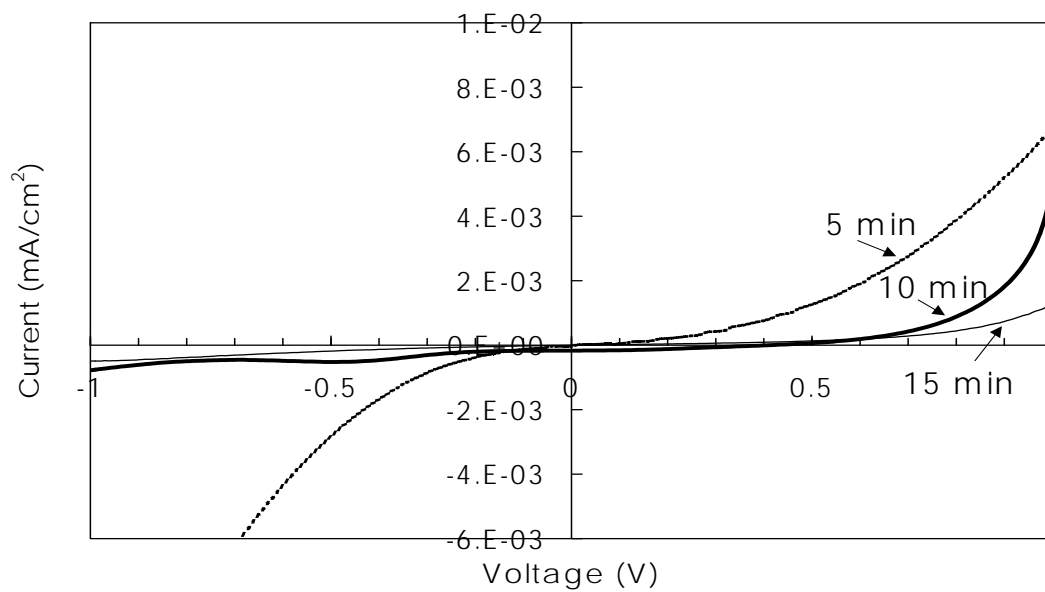


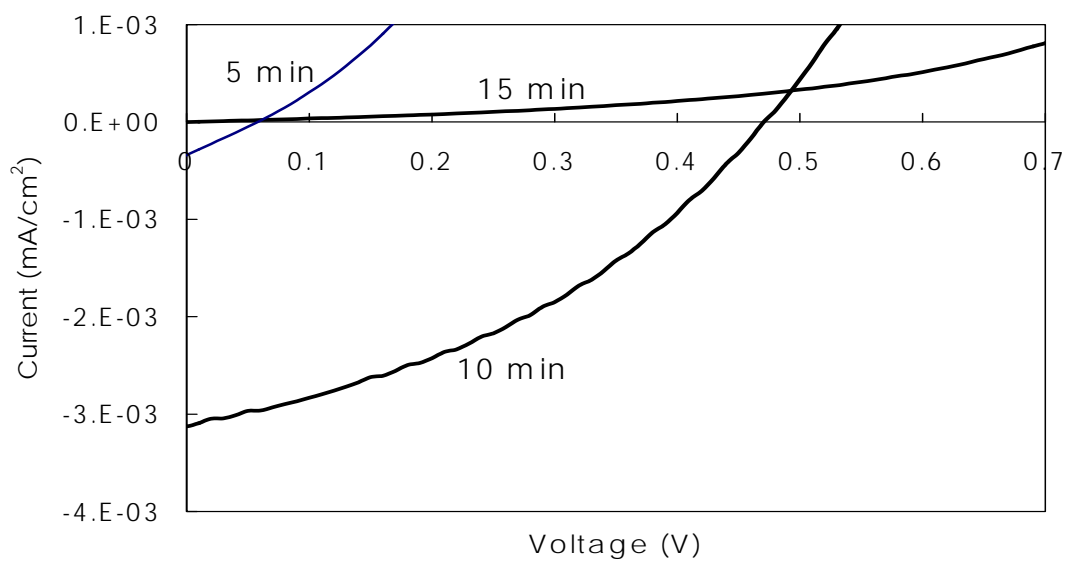
Figure 3



(a)



(b)



(c)

Figure 4