**NEW APPROACH FOR GENERATING Cu2O/TiO2 COMPOSITE FILMS FOR SOLAR CELL APPLICATIONS**

Rosdi Zainun Ayib, Tomoya Sakamoto, Mohd Noor Uzer, Rusop Mohamad, Masaya Ichimura

**Journal or Publication Title**

Materials Letters

**Volume**

66

**Number**

1

**Page Range**

254-256

**Year**

2012-01-01

**URL**

http://id.nii.ac.jp/1476/00005595/

doi: 10.1016/j.matlet.2011.08.032 (http://dx.doi.org/10.1016/j.matlet.2011.08.032)

(c)Elsevier. NOTICE: this is the author’s version of a work that was accepted for publication in Materials Letters. Changes resulting from the publishing process, such as peer review, editing, corrections, structural formatting, and other quality control mechanisms may not be reflected in this document. Changes may have been made to this work since it was submitted for publication. A definitive version was subsequently published in Materials Letters [See also CITATION, DOI].
NEW APPROACH FOR GENERATING Cu₂O/TiO₂ COMPOSITE FILMS FOR SOLAR CELL APPLICATIONS

Ayib Rosdi Zainun*, 1, 2, 3, Sakamoto Tomoya1, Uzer Mohd Noor2, Mohamad Rusop2, Ichimura Masaya1

1Department of Engineering Physics, Electronics and Mechanics, Nagoya Institute of Technology
2Solar Cell Laboratory, Faculty of Electrical Engineering, Universiti Teknologi MARA (UiTM), Shah Alam, Selangor, Malaysia.
3Faculty of Electrical and Electronics Engineering, Universiti Malaysia Pahang (UMP) Kuantan, Pahang, Malaysia.

Tel: 609-4242031, Fax: 609-4242032.
*E-mail address: ayibrsd@yahoo.com, ayib@ump.edu.my

Abstract

In this paper, Cu₂O was studied as a photon absorber for solar cell applications. Cu₂O was deposited on a TiO₂ film using the electrochemical deposition (ECD) method. Based on the physical appearance of the samples, the particles of Cu₂O seemed to penetrate the TiO₂ film and were primarily deposited near the TiO₂/substrate interface rather than on the TiO₂ film surface. This method could be one way to generate a p-n bulk-heterojunction interface. The film was confirmed to be a Cu₂O/TiO₂ 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**

TiO$_2$ 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 TiO$_2$ 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 CuInS$_2$, 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 TiO$_2$. 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 TiO$_2$/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 TiO$_2$/CuInS$_2$ 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 (Cu$_2$O) as a p-type solar cell material to be deposited on TiO$_2$ for solar cell applications. In this study, Cu$_2$O was used as a photon absorber. Cu$_2$O, 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 Cu$_2$O/TiO$_2$ heterojunction thin film and observed a photoresponse in a photoelectrochemical cell [15]. Li et al. prepared core shell Cu$_2$O/TiO$_2$ solar cell with an efficiency ~0.01%
The combination of Cu$_2$O and TiO$_2$ could contribute to efficient photoelectric conversion. In this research, Cu$_2$O/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$_2$O 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$_2$O 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 mA/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$_2$O was deposited, the top surface remained white, while the bottom side (the substrate side) turned orange (the color of Cu$_2$O). Thus, the Cu$_2$O 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$_2$O gradually filled the porous matrix of TiO$_2$ from the bottom, as shown in Figure 1 (d). When Cu$_2$O, was deposited, it is likely that the deposition solution easily penetrated the TiO$_2$ film. For Cu$_2$O 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 Cu₂O was preferentially deposited near the interface rather than on the top surface.

Figure 2 shows X-ray diffraction patterns for the Cu₂O, TiO₂, and Cu₂O/TiO₂ composite films. All of the peaks observed for TiO₂ can be attributed to the TiO₂ anatase structure, and the peaks observed for Cu₂O can be attributed to the Cu₂O cubic structure. For the composite film, in addition to the TiO₂ peaks, Cu₂O peaks were also observed.

Figure 3 shows optical transmission spectra for the TiO₂, Cu₂O, and Cu₂O/TiO₂ composite films. The Cu₂O film has an absorption edge around 570 nm, which corresponds to its band gap of 2.1 eV. The TiO₂ 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 Cu₂O.

For the I-V characterization, indium was evaporated as shown in Figure 4 (a). Figure 4 (b) shows the photovoltaic behavior of the Cu₂O/TiO₂ composite films measured during illumination through the FTO glass substrate. Three samples with different Cu₂O deposition times were prepared and measured. The AM1.5 light intensity was maintained at 100 mW/cm² for all of the measurements. For the 10 min deposition sample, the short-circuit current was 0.0031 mA/cm², the open-circuit voltage was 0.47 V, and the efficiency was 5x10⁻⁴ %. 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 TiO₂ and the interface side was primarily comprised of Cu₂O, 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 Cu₂O/TiO₂ 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
Cu$_2$O films were deposited by ECD on TiO$_2$ 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.

**Acknowledgements**

We extend a special thanks to all members of Prof. Ichimura’s lab for their useful discussion, cooperation, support and assistance in completing the research that led to this paper.

**References**

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

**Figure 2**: X-ray diffraction patterns of (a) Cu$_2$O, (b) TiO$_2$ and (c) Cu$_2$O/TiO$_2$ composite films.

**Figure 3**: Transmission spectra for (a) Cu$_2$O (b) TiO$_2$ and (c) the Cu$_2$O/TiO$_2$ composite films.

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

Figure 3
Figure 4