INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2018) 1–14

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/he

Mechanistic investigation on tuning the conductivity type of cuprous oxide (Cu_2O) thin films via deposition potential

Juan Han [a,1,2], *Jing Chang* [a,1], *Rong Wei* [a], *Xiaohui Ning* [a], *Jian Li* [a], *Zuoxi Li* [a], *Huilin Guo* [a], *Ying Yang* [a,b,*]

[a] *Shaanxi Provincial Key Laboratory of Electroanalytical Chemistry, Key Laboratory of Synthetic and Natural Functional Molecule Chemistry of the Ministry of Education, Institute of Analytical Science, College of Chemistry & Materials Science, Northwest University, Xi'an, Shaanxi 710127, PR China*

[b] *International Research Center for Renewable Energy, State Key Laboratory of Multiphase Flow in Power Engineering, Xi'an Jiaotong University, Xi'an, Shaanxi 710049, PR China*

ARTICLE INFO

Article history:
Received 22 January 2018
Received in revised form
14 February 2018
Accepted 19 February 2018
Available online xxx

Keywords:
Conductivity type
Cuprous oxide (Cu_2O)
Thin film
Semiconductor
Photoelectrochemistry

ABSTRACT

The conductivity type of cuprous oxide (Cu_2O) thin films is tuned by controlling the deposition potential of an electrochemical process in an acid cupric acetate solution containing sodium dodecyl sulfate. The morphology and chemical composition of the deposited Cu_2O films are studied by SEM, XRD and XPS. The change of the conductivity type of Cu_2O films is further studied through zero-bias photocurrent and Mott-Schottky measurements. The results indicate that the Cu_2O films behave as n-type semiconductors when the overpotentials are low (potentials higher than −0.05 V) and p-type semiconductors when the overpotentials are high (potentials lower than −0.10 V). The transformation of conductivity from n-type to p-type comes from the competition reactions between forming Cu_2O and forming metallic Cu from Cu^{2+}. When the potential is lower than −0.10 V, most of Cu^{2+} are consumed by the growth of metallic Cu at the film/solution interface, so that the Cu^{2+} provided to grow Cu_2O film are insufficient and copper vacancies form in the film, leading to the p-type conductivity.

Introduction

Cuprous oxide (Cu_2O) has attracted a great deal of attention because of its direct bandgap of around 2 eV for broad applications in photoelectrochemical (PEC) CO_2 utilization [1–5], PEC hydrogen production [6–12], photovoltaic (PV) cell [13–21], detector and sensor [22–24]. Cu_2O with different conductivity type (n-type or p-type) plays different role in these applications, for instance, a layer of n-type Cu_2O combining with a layer of p-type Cu_2O forms a homojunction for fabricating PV cell, while n-type Cu_2O films and p-type Cu_2O films can be used as photoanode and photocathode in

* *Corresponding author*. Shaanxi Provincial Key Laboratory of Electroanalytical Chemistry, Key Laboratory of Synthetic and Natural Functional Molecule Chemistry of the Ministry of Education, Institute of Analytical Science, College of Chemistry & Materials Science, Northwest University, Xi'an, Shaanxi 710127, PR China.
E-mail address: yingyang@nwu.edu.cn (Y. Yang).
[1] These authors contributed equally to this work.
[2] Present address: Chemistry Department, University of North Dakota, Grand Forks, ND58202, USA.

https://doi.org/10.1016/j.ijhydene.2018.02.121
0360-3199/

PEC CO_2 reduction, respectively. The conductivity type of Cu_2O can be controlled through thermal treatment [25–27] or electrochemical deposition process [19,28–36]. For example, Siripala et al. [25] found that the electrodeposited Cu_2O films behaved as n-type semiconductors when they were annealed below 300 °C, while the films behaved as p-type semiconductors when annealed above 300 °C owing to the formation of cupric oxide (CuO) in the films. Wang et al. [27] reported a similar phenomenon in which the electrodeposited n-type Cu_2O films were converted to p-type semiconductors covered with a layer of CuO after they were annealed at 400 °C in air. The tunable conductivity type of Cu_2O has also been extensively studied through the control of the electrodeposition parameters, such as pH of plating solution, cupric ions (Cu^{2+}) concentration, and surfactant concentration. The Cu_2O films deposited in acidic solutions generally exhibit n-type conductivity, while those deposited in basic solutions exhibit p-type conductivity [19,28–30,37,38]. For instance, McShane and Choi [28] and Jiang et al. [30] deposited n-type Cu_2O films in cupric acetate solutions at pH 4.9 and p-type Cu_2O films in cupric sulphate solutions at pH 7.0–9.0; Liau et al. [29] fabricated n-type and p-type Cu_2O films in cupric acetate solutions at pH 4.9 and pH 11, respectively. The conductivity type of Cu_2O films can be controlled by the concentration of Cu^{2+} in plating solution. A previous report [39] indicated that p-type Cu_2O was deposited because of the formation of copper vacancies in the film when the Cu^{2+} concentration was less than 5 mM in cupric acetate solution, while n-type Cu_2O was synthesized when the Cu^{2+} concentration was more than 8 mM. In addition, surfactants sodium dodecyl sulfate (SDS) can be used to control the conductivity type of Cu_2O films through an electrochemical process [40]. Besides, in previous report [41], we showed that semiconducting conductivity of Cu_2O could be tuned through changing deposition potential, however, the

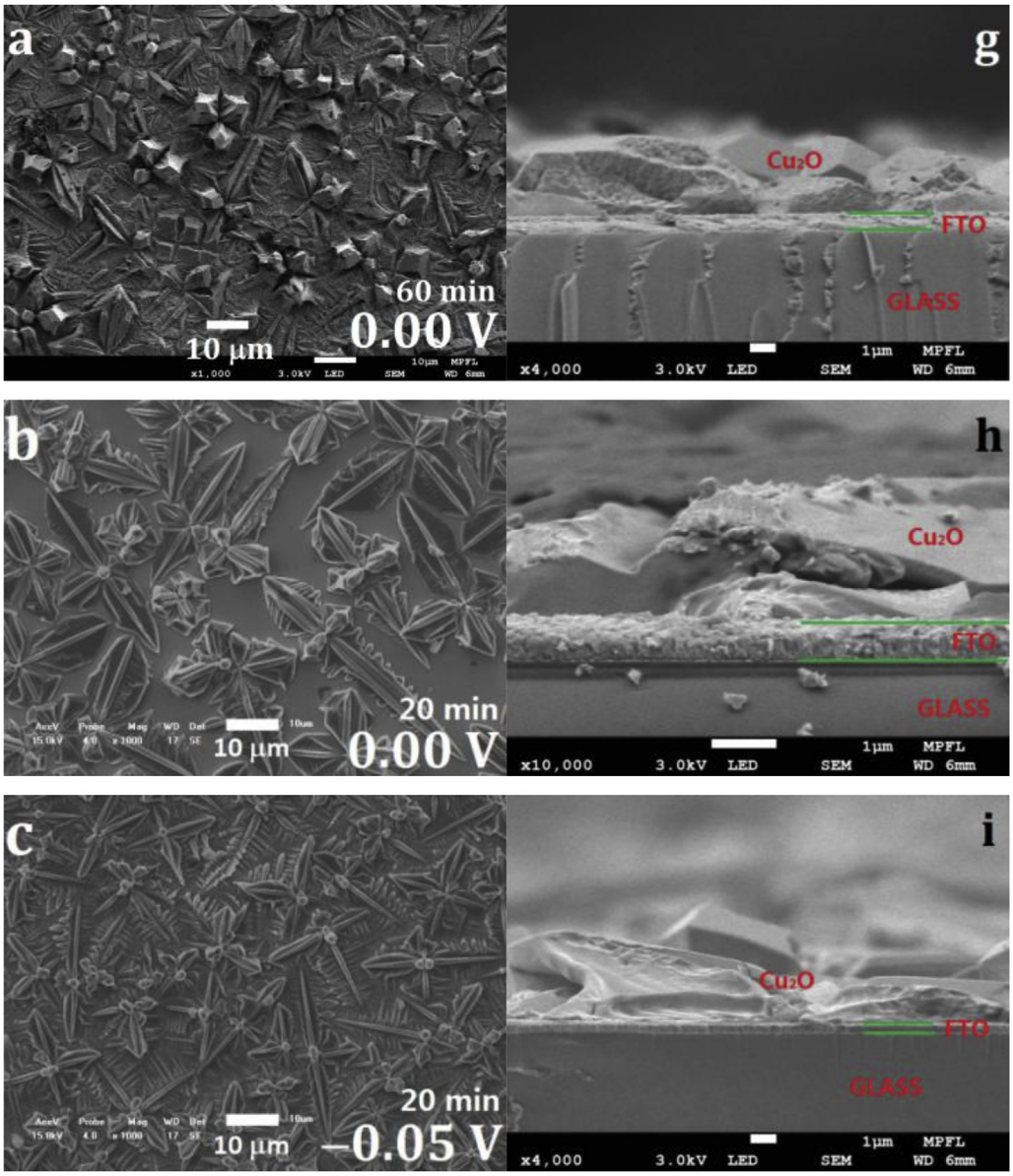

Fig. 1 – Surface morphology (a–f) and cross section (g–l) of the Cu_2O films deposited at (a, g) 0.00 V for 60 min, (b, h) 0.00 V for 20 min, (c, i) −0.05 V for 20 min, (d, j) −0.10 V for 20 min, (e, k) −0.20 V for 20 min, and (f, l) −0.30 V for 20 min.

Please cite this article in press as: Han J, et al., Mechanistic investigation on tuning the conductivity type of cuprous oxide (Cu_2O) thin films via deposition potential, International Journal of Hydrogen Energy (2018), https://doi.org/10.1016/j.ijhydene.2018.02.121