



ELSEVIER

Contents lists available at ScienceDirect

## Solar Energy Materials &amp; Solar Cells

journal homepage: [www.elsevier.com/locate/solmat](http://www.elsevier.com/locate/solmat)Structural and electrical properties of CuO films and *n*-ZnO/*p*-CuO heterojunctions prepared by chemical bath deposition based techniqueTomoaki Terasako <sup>a,\*</sup>, Toshihiro Murakami <sup>a</sup>, Atsushi Hyodou <sup>b</sup>, Sho Shirakata <sup>a</sup><sup>a</sup> Graduate School of Science & Engineering, Ehime University, 3 Bunkyo-cho, Matsuyama, Ehime 790–8577, Japan<sup>b</sup> Faculty of Engineering, Ehime University, 3 Bunkyo-cho, Matsuyama, Ehime 790–8577, Japan

## ARTICLE INFO

## Article history:

Received 23 May 2014

Received in revised form

3 July 2014

Accepted 20 August 2014

## Keywords:

ZnO

CuO

Chemical bath deposition

Heterojunction

## ABSTRACT

Structural and electrical properties of the CuO films and the ZnO/CuO heterojunctions prepared by chemical bath deposition (CBD) technique involving thermal annealing process were studied by scanning electron microscope observation, X-ray diffraction, current density-voltage (*J*-*V*) and capacitance-voltage (*C*-*V*) measurements. The as-grown CuO films showed *p*-type conduction after annealing in the air at temperatures ( $T_A$ ) ranging from 200 to 300 °C. The *n*-ZnO/*p*-CuO heterojunctions were composed of the columnar CuO grains and the ZnO nanorods (NRs) and their *J*-*V* curves exhibited rectifying characteristics with large diode ideality factors (*n*) and leakage currents. The insertion of the ZnO intermediate layer prepared by dip-coating (denoted by “Dip-coating ZnO”) between the ZnO and CuO layers was found to be effective for reducing the *n* value and suppressing the leakage current. The threshold voltage ( $V_{th}$ ), built-in potential ( $V_{bi}$ ) and *n* value of the ZnO/Dip-coating ZnO/CuO heterojunction were strongly dependent on  $T_A$  and showed minima around  $T_A = 250$ – $300$  °C. Taking into account the fact that the rectification ratios of the forward current to the reverse current were very low at the same  $T_A$  region, the low  $V_{th}$  and  $V_{bi}$  values are attributed to the tunneling process through the interface states introduced by the structural imperfection.

© 2014 Elsevier B.V. All rights reserved.

## 1. Introduction

Tin doped indium oxide ( $\text{In}_2\text{O}_3:\text{Sn}$ , ITO) films are widely used as transparent conducting oxide (TCO) films in the electrodes of flat panel displays and in the window layers of thin film solar cells. However, the alternative TCO materials are required because of the limited availability of In, one of the rare-metals. Zinc oxide (ZnO) with a hexagonal wurtzite structure has the band gap energy of 3.37 eV, which is transparent to visible light. A variety of growth techniques has been utilized for preparing ZnO films so far [1]. It is also known that ZnO films doped with the group III elements (B, Al, Ga and In) or the group VII element (F) show low-resistivity *n*-type conduction. Therefore, ZnO is one of the most conceivable candidates for the alternative TCO material [2]. Moreover, ZnO is abundant, inexpensive and non-toxic. On the other hand, it is difficult to obtain high quality *p*-type ZnO films reproducibly because of the self compensation effect that a crystal lowers its energy by forming point defects and/or complex defects to counter the effects of a dopant.

Cupric oxide (CuO) with a monoclinic structure and cuprous oxide ( $\text{Cu}_2\text{O}$ ) with a cubic structure, stable phases of the well-established

copper-oxide compounds, exhibit naturally *p*-type conduction derived from copper vacancies ( $V_{Cu}$ ). The band gap energies of CuO and  $\text{Cu}_2\text{O}$  have been reported to be  $\sim 1.35$  eV and  $\sim 2.1$  eV, respectively [3]. Up to now, there are some reports on the successful growth of *p*- $\text{Cu}_2\text{O}/n$ -ZnO heterojunctions and solar cell performances. The energy conversion efficiency of 3.83% was achieved on the heterojunction fabricated by depositing the ZnO layer on the thermal oxidized  $\text{Cu}_2\text{O}$  layer by pulse laser deposition (PLD) [4]. Moreover, the insertion of the  $\text{Ga}_2\text{O}_3$  layer between the  $\text{Cu}_2\text{O}$  and ZnO layers was found to improve the energy conversion efficiency effectively [5]. According to the Shockley-Queisser limitation assuming single *pn* junction solar cells, however, the maximum energy conversion efficiency is expected to be achieved at the band gap energy of  $\sim 1.4$  eV, which is very close to the direct band gap energy of CuO rather than that of  $\text{Cu}_2\text{O}$ . Rectifying behavior was observed on the current (*I*)–voltage (*V*) characteristics of the *p*-CuO/*n*-ZnO heterojunctions prepared by directly bonding of ZnO and CuO sintered bodies [6] and by electrodeposition [7]. For the later heterojunction, a low energy conversion efficiency of  $1.1 \times 10^{-4}\%$  was obtained. Recently, Saji et al. have reported the successful growth of the CuO/*i*-ZnO/ZnO:Al heterojunction with the energy conversion efficiency of  $3 \times 10^{-4}\%$  by rf magnetron sputtering [8].

As with the case of ZnO, CuO films have been prepared by various methods, such as chemical vapor deposition (CVD) [9,10], spray pyrolysis [11], dip-coating [12], electrospun [13], PLD [14,15]

\* Corresponding author. Tel.: +81 8 9 927 9789; fax: +81 89 927 9790.

E-mail address: [terasako.tomoaki.mz@ehime-u.ac.jp](mailto:terasako.tomoaki.mz@ehime-u.ac.jp) (T. Terasako).

and chemical bath deposition (CBD) [16] so far. Among these growth methods, we have paid attention to CBD which is based on controlled precipitation on a substrate via hydrolysis and/or condensation of metal ions and/or complexes from aqueous solution. The CBD method is performed at temperatures typically lower than 100 °C, which allows us to use polymers as substrate materials. In our previous paper, the shape controllability of vertically aligned ZnO nanorods (NRs) by the CBD using ZnCl<sub>2</sub> and zinc acetate dihydrate [ZnAc, (CH<sub>3</sub>COO)<sub>2</sub>Zn · 2 H<sub>2</sub>O] as source materials and the optical properties of the ZnO NRs [17] have been reported.

In the present paper, the fabrication of *p*-CuO films and *n*-ZnO/*p*-CuO based heterojunctions by CBD technique accompanied by thermal annealing process, and their structural and electrical properties will be discussed in terms of the post-annealing temperature for CuO layer. To improve the interfacial properties, the insertion of intermediate layers between the CuO and ZnO layers will be also examined.

## 2. Experimental

### 2.1. Sample preparation

A flow chart for the fabrications of *n*-ZnO/*p*-CuO based heterojunctions with the substrate configuration is shown in Fig. 1. Commercial Au (200 nm) /Ti (50 nm)/Si wafers (Kyodo International) were used as substrate materials. The Au layer acts as not only the seed layer for the CBD of the CuO layer, but also the back contact electrode. The alkali-free glass substrates coated with the Au layers were also used for preparing single CuO films. The CBD of the CuO layers was performed on the Au seed layers using the aqueous solution of Cu(NO<sub>3</sub>)<sub>2</sub> · 3 H<sub>2</sub>O (denoted by “CuNA”) with the concentration of 0.05 M. The pH value of the CuNA aqueous solution was adjusted to be 10 by the use of ammonia solution (28%). The CuNA aqueous solution was poured into a Pyrex glass beaker. The beaker was placed in the water bath. The bath temperature (*T<sub>B</sub>*) for the CuO layer was maintained at 90 °C. The substrate was suspended in the aqueous solution. During the growth process, the solution was stirred with a magnetic stirrer.

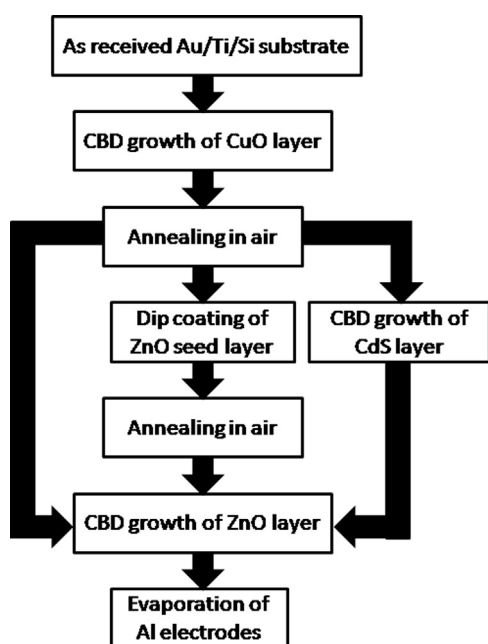


Fig. 1. Flow chart for the fabrications of *n*-ZnO/*p*-CuO based heterojunctions with substrate configuration.

Growth time (*t<sub>g</sub>*) for the CuO layer was 60 min. Post annealing procedure was performed for the as-grown CuO film in the air for 10 min at annealing temperatures (*T<sub>A</sub>*) ranging from 150 to 350 °C. The CBD ZnO layers were grown on the annealed CuO layer directly or on the intermediate layer deposited on the annealed CuO layer. The intermediate layers attempted in this study are as follows: ① ZnO layers grown by dip coating (denoted by “Dip-coating ZnO”) using the aqueous solution of (CH<sub>3</sub>COO)<sub>2</sub>Zn · 2 H<sub>2</sub>O (denoted by “ZnAc”) and ② CdS layers grown by CBD using cadmium sulfate (CdSO<sub>4</sub>) and thiourea as precursors. The Dip-coating ZnO layers were prepared by repeating the immersion of the CuO films in the 0.05 M ZnAc solution at ~20 °C for 3 sec five times followed by thermal annealing at 250 °C in the air for 10 min. The CdS intermediate layers were grown by CBD using the mixed aqueous solution of 1.5 mM CdSO<sub>4</sub>, 0.075 M thiourea and 2 M ammonia solution at *T<sub>B</sub>*=75 °C for 7 min. The CBD ZnO layers were synthesized from the ZnAc aqueous solution of 0.01 M whose pH value was adjusted to be 10.5 by adding ammonia solution. The growth apparatus and procedure for the CBD ZnO layers were the same for those for the CBD CuO layers. The CBDs of the ZnO layers were performed at *T<sub>B</sub>*=70 °C for *t<sub>g</sub>*=20 min. The aluminum (Al) surface electrodes were formed by vacuum evaporation.

### 2.2. Characterizations

The crystalline structure was characterized by X-ray diffraction (XRD) method using the Cu K $\alpha$  radiation with a conventional  $\theta$ -2  $\theta$  goniometer (Philips, PW1820/00). Surface and cross-sectional morphologies were examined by scanning electron microscope (SEM; Hitachi, S-3100). Conduction type was checked by thermopower measurements using our home-made apparatus. Electrical properties of the fabricated *n*-ZnO/*p*-CuO heterojunctions were characterized by current density (*J*)-voltage (*V*) measurements using digital multimeters (Advantest, R6451A and R8240) and a DC stabilized power source (Kenwood, PA70-1A) and by capacitance (*C*)-voltage (*V*) measurements under the frequency of 1 MHz using a capacitance meter (Hioki, 3532-50) and a digital multimeter (Yokogawa, 7651).

## 3. Results and discussion

### 3.1. Structural and electrical properties of CuO films

Fig. 2 shows XRD patterns of the CuO/Au/glass films annealed at *T<sub>A</sub>*=200, 350 and 500 °C in the air for 10 min, together with that of the as-grown film. In the range from 32 to 55°, the (110), (0 0 2) and (020) peaks of CuO and the strong (1 1 1) peak of Au can be seen. The inset shows variations of the intensity and full-width at half-maximum (FWHM) value of the CuO (0 0 2) peak as a function of annealing temperature (*T<sub>A</sub>*). The intensity of the CuO (0 0 2) peak increases, whereas its FWHM value decreases with increasing *T<sub>A</sub>*. This finding suggests that the post annealing in the air is effective for improving the crystalline quality. The intensity ratio of the CuO (0 0 2) peak to the summation of those of all the observed CuO peaks, indicating the degree of crystallographic orientation of the film, was independent of *T<sub>A</sub>*.

On the same CuO/Au/Ti/Si film, the resistivity measured between the Au electrodes formed on the surface (surface Au electrodes) was almost twice of that between the surface and back Au electrodes. This result indicates that, when the resistivity measurement is performed between the surface Au electrodes, most of current flow via the back Au contact, that is to say the resistivity of the CuO layer in the surface direction is extremely larger than that in the thickness direction. In other words, the

Download English Version:

<https://daneshyari.com/en/article/6535351>

Download Persian Version:

<https://daneshyari.com/article/6535351>

[Daneshyari.com](https://daneshyari.com)