Journal of New Materials for Electrochemical Systems 17, 45-48 (2014)

Microstructure Properties of ZnO/ Indium Tin Oxide and ZnO/$CuInSe_2$ grown by Electrochemical Deposition

Hsiang Chen[1,*], Yih-Min Yeh[2], Yun Ti Chen[1], Chian You Chen[1], Sheng-Hsin Wang[1], Li-Chen Chu[1], Ren Guei Ueng[2], Hsi-Wen Yu[1] and Sheng-Ting Huang[1]

[1]Department of Applied Materials and Optoelectronic Engineering, National Chi Nan University, Puli, Taiwan, R.O.C.
[2]Graduate School of Opto-Mechatronics and Materials, WuFeng University, Minhsiung, Taiwan, R.O.C.

Received: June 25, 2013, Accepted: September 25, 2013, Available online: November 28, 2013

Abstract: *In this research, we grew a ZnO film as a buffer layer on indium tin oxide (ITO) substrates and $CuInSe_2$/ITO (CIS/ITO) substrates by electrochemical deposition. To examine material quality of ZnO films, multiple material and optical analyses including scanning electron microscope images, electron probe microanalyzer images, UV-VIS, and x-ray diffraction were conducted. The results indicate that an appropriate amount of H_2O_2 might enhance the growth of ZnO films on the ITO substrate. Furthermore, triethanolamine addition might suppress the reaction between KCl and the CIS substrate to enhance the growth of the ZnO film on the CIS substrate. The ZnO/CIS structure may replace the toxic CdS/CIS structure for the further development for the CIS solar cell.*

Keywords: ZnO, $CuInSe_2$, H_2O_2, triethanolamine, electrochemical deposition

1. INTRODUCTION

Owing to global warming and increase of oil prices, solar cells have been intensively studied as alternative energy source. Among various kinds of solar cells, $CuInSe_2$ (CIS) based solar cells have attracted growing attention because of their cheap price, high absorption coefficient, and long life [1]. ZnO, a well conducting transparent oxide, has been incorporated to form a buffer layer with $CuInSe_2$ to replace the toxic CdS layer [2]. To grow ZnO on top of the CIS structure, chemical bath deposition (CBD) [3], chemical vapor deposition (CVD) [4], atomic layer deposition (ALD) [5], and electrochemical deposition (ECD) [2] have been reported. Compared with other fabrication methods, ECD has advantages of low temperature process, large area manufacturing, low cost and simple fabrication [6]. In this research, we grew ZnO film by ECD on indium tin oxide (ITO) [7, 8] and CIS substrate [2], respectively. To improve material quality of the deposited ZnO on ITO and CIS, hydrogen peroxide (H_2O_2) as oxygen precursor has been included in the plating solution [9]. In contrast to previous studies [10, 11], we investigated the influence of H_2O_2 concentration. Moreover, CIS substrates with and without triethanolamine (TEA) addition were examined [12]. To characterize the ZnO film with different growth conditions, multiple material analysis techniques [13] including X-ray diffraction (XRD) spectra, scanning electron microscopy (SEM), and electron probe microanalyzer (EPMA) images were taken. Moreover, the transmittance of the ZnO /ITO structure was measured by UV-VIS [7]. The experimental results indicate that an appropriate concentration of H_2O_2 could enhance the crystalline structure of the ZnO film on ITO and the transmittance could reach around 90% for the wavelength over 650 nm [7, 14]. After finding the growth the deposition parameters to grow ZnO on ITO substrate, we used the same parameters to deposit good crystallized ZnO on CIS substrate. The results reveal that incorporation of TEA could suppress the reaction between KCl in electrolyte and the CIS substrate, which might cause peeling of ZnO during growth.

2. EXPERIMETNAL

2. 1. ECD plating solution and system

To grow a ZnO buffer layer on top of the CIS film, we first deposited ZnO films on ITO substrates and then on CIS substrates. The size of the ITO substrate was 20 mm × 20 mm. As for the CIS film, the film was grown by electro-deposition and the detailed process can be seen in our previous research [15, 16]. The ECD system consisted of ITO or CIS as the working electrode, Pt as

*To whom correspondence should be addressed: Email: hchen@ncnu.edu.tw
Phone:

the counter electrode, and Ag/AgCl as the reference electrode. The deposition parameters are shown in Table 1 [17]. Before the deposition process, H_2O_2 was added into the plating solution. To study the growth condition and optical properties of the ZnO film, multiple material analyses techniques including XRD spectra, SEM, and EPMA to characterize the material properties and UV-VIS to investigate the optical transmittance.

2.2. Reaction of electrochemical deposition of ZnO thin films

In this experiment, we used a fixed voltage to deposit zinc oxide. The plating solution consisted of $ZnCl_2$, 30% of H_2O_2 as the oxygen precursor, and 0.1M of KCl as an auxiliary electrolyte to improve the conductivity of the electrolyte. With an oxygen atom from the oxygen precursor H_2O_2, the film might contain a mixture of zinc hydroxide (ZnO-$Zn(OH)_2$ mixture). The chemical reaction formula step by step are as follows [9]:

$$H_2O_2 + 2e^- \rightarrow 2OH^- \quad (1)$$

Formula (1): The reduction reaction of hydrogen peroxide occurred in cathode.

$$2OH^- + Zn^{2+} \rightarrow Zn(OH)_2 \quad (2)$$

Formula (2): The hydrogen peroxide reacted with the zinc ions in the solution to produce zinc hydroxide.

$$Zn(OH)_2 \rightarrow ZnO + H_2O \quad (3)$$

Formula (3): A dehydration reaction occurred in a solution with a temperature higher than 50℃.

Formula (4): The total reaction is as follows:

$$Zn^{2+} + H_2O_2 + 2e^- \rightarrow ZnO + H_2O \quad (4)$$

3. RESULTS AND DISCUSSION

We first investigated the deposited ZnO film on the ITO substrate with XRD, UV-VIS, and SEM analyses. To examine the crystalline structure of the film, XRD of the ZnO film deposited in solutions with H_2O_2 concentrations of 5, 10, 15mM are shown in Fig. 1. The XRD spectra indicate that stronger ZnO crystalline phases could be obtained as the H_2O_2 concentration was higher than 10 mM. To evaluate the transmittance of the ZnO film, UV-VIS was used to measure the transmittance. As shown in Fig. 2, the film deposited in a solution with the H_2O_2 concentration of 10 mM had the highest transmittance. Therefore, the deposition condition with the H_2O_2 concentration of 10 mM might be an appropriate condition to grow ZnO on the CIS/ITO substrate. A SEM image of a ZnO film deposited on ITO substrate in a solution with the H_2O_2 concentration of 10 mM are shown in Fig. 3 (a), indicating that a ZnO film with a good material quality might be formed. To further analyze the film, oxygen and zinc element mapping were performed by EPMA as shown in Fig. 3 (b) and (c). The EPMA results reveal that a uniform ZnO film might be formed based on the O and Zn element mapping.

Table 1. ZnO deposition conditions

ZnO deposition parameters	
$ZnCl_2$ Concentration	10mM
KCl Concentration	0.1M
H_2O_2 Concentration	5mM~15mM
pH values	5~8
Deposition Voltage	-1.75V
Current Density	0.015ASD~0.03ASD
Deposition Time	10 min
Temperature	75℃

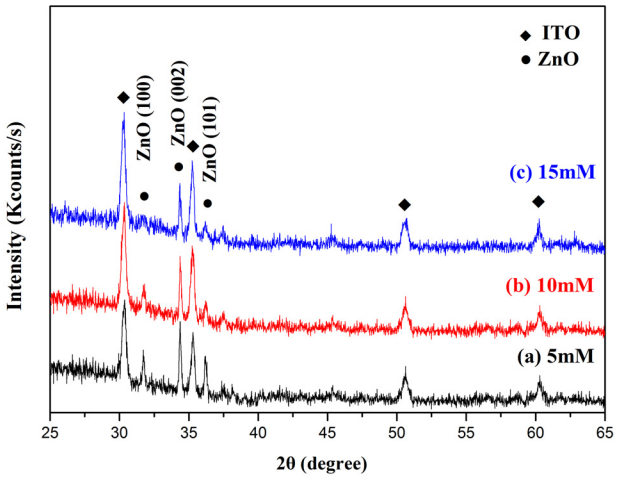

Figure 1. XRD analyses of the ZnO film on ITO deposited in solutions with H_2O_2 concentrations of 5, 10, and 15mM.

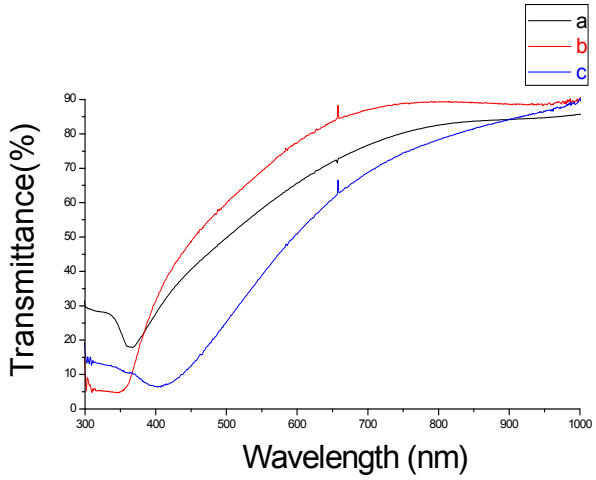

Figure 2. Transmittance of ZnO films in solutions with H_2O_2 concentrations of (a) 5mM, (b)10mM, (c) 15mM.

After an appropriate condition to grow ZnO films on the ITO substrate was found, we used these deposition parameters to grow ZnO films on the CIS substrate. The CIS substrate was formed by growing the CIS film on the ITO substrate [15]. Since the CIS film on the substrate was also grown by ECD, the CIS substrate prepared with and without TEA addition exhibited two distinct behaviors.

The CIS substrate with and without TEA addition of a concentration of 3M are shown in Fig. 4 (a) and (b). To compare

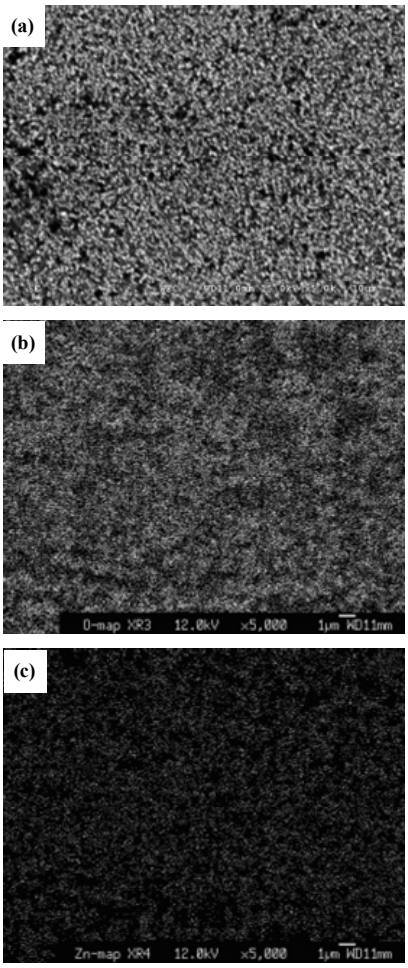

Figure 3. (a) A SEM image of a ZnO film on the ITO substrate in a solution with a H2O2 concentration of 10mM. EPMA analyses for the film with (b) O mapping and (c) Zn mapping. (The scale of (a) is the same as (b) and (c))

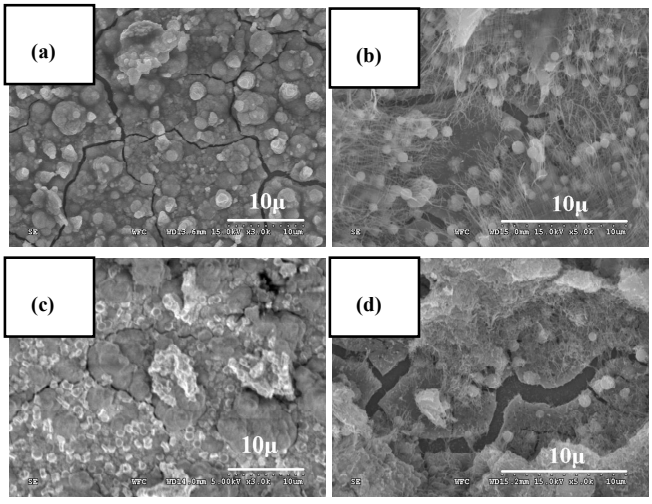

Figure 4. SEM images of (a) a CIS film with adding TEA. (b)a CIS film without adding TEA (c) a ZnO film deposited on CIS for 10 minutes with adding TEA and (d) without adding TEA.

ZnO films grown on the CIS substrate, SEM images of a ZnO film deposited on CIS for 10 minutes with adding TEA and without adding TEA are shown in Fig. 4(c) and (d). It can be seen that a ZnO film with a better growth on the CIS substrate containing TEA. By contrast, cracks were enlarged and a ZnO film with a poor material quality was grown on the CIS substrate without TEA. To investigate the origin, XRD was used to study the crystalline structure of the ZnO film on the CIS substrate with and without TEA. Fig. 5 (a) and (b) shows XRD spectra for ZnO film deposited on CIS for 10 minutes with adding TEA and without adding TEA. In the spectra, the crystalline phases of ZnO are (100), (002) and (101), and (102) [18] . CIS phases are (112), (220), and (312) [15] on the ITO substrate [19]. Strong ZnO crystalline structures can be seen on the CIS substrate with TEA as shown in Fig. 5(b). By contrast, ZnO crystalline phases can hardly be observed on the CIS substrate without TEA as shown in Fig. 5(b). In addition, an undesired KSe_2 peak can be seen on the XRD spectra. The XRD results imply that K^+ from KCl in the electrolyte might react with Se in the CIS substrate and the reaction might cause peeling of the ZnO and cracking of the substrate. Moreover, TEA might suppress the reaction between KCl and the substrate. Our further research confirms the statement.

We grew ZnO films on the CIS substrate containing a higher concentration of TEA (4.7M) for 10 , 30, and 60 min as shown in

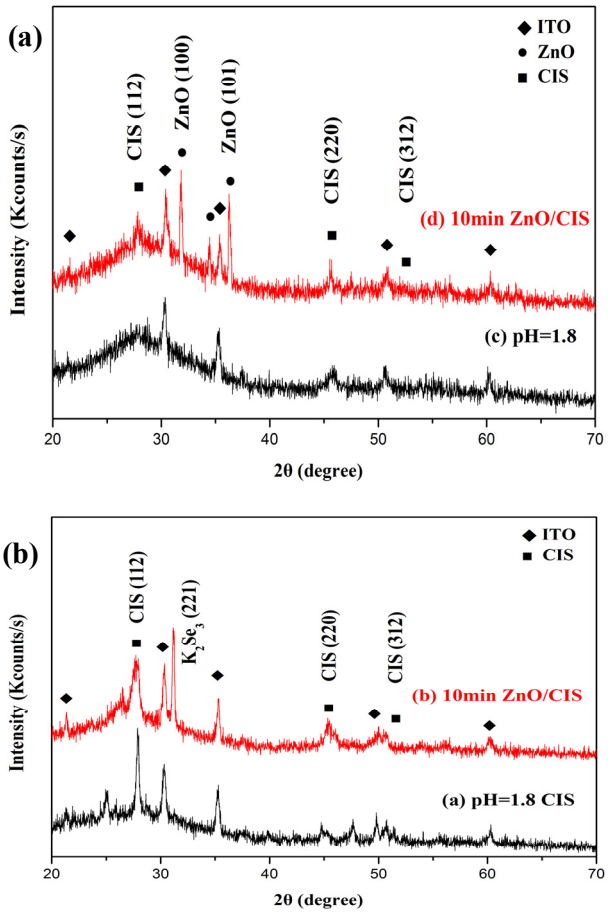

Figure 5. (a) XRD patterns of ZnO deposited on CIS for 10 minutes with adding TEA (3M). (b) XRD patterns of ZnO deposited on CIS for 10 minutes without adding TEA.

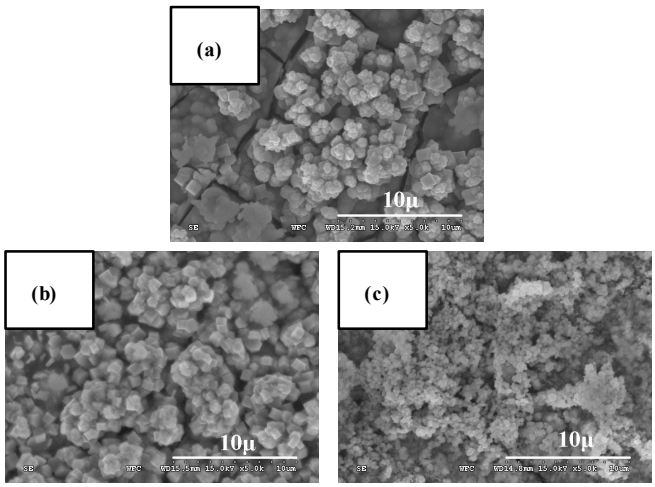

Figure 6. SEM images of ZnO deposited on CIS at pH=1.8 with adding TEA (4.7M) for (a) 10 minutes, (b) 30 minutes, and (c) 60 minutes.

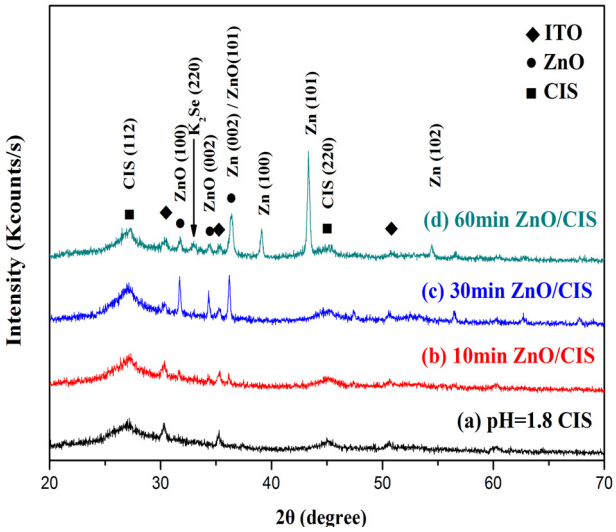

Figure 7. XRD patterns of ZnO deposited on CIS with adding TEA (4.7M) for (b) 10 minutes, (c) 30 minutes and (d) 60 minutes. (◆ : ITO,■: Zinc oxide peak, ♥ : CIS peak)

Fig. 6 (a), (b), and (c). Compared with the CIS substrate with TEA addition in a lower concentration of 3M as shown in Fig. 4(c), the ZnO film exhibited a better material quality as shown in Fig. 6 (a). As the deposition time increased to 60 min, the morphology became worse. To study the origin, XRD of ZnO films grown on the CIS substrate containing a TEA concentration of 4.7M are shown in Fig. 7. As the deposition time increased from 0 to 30 min, the ZnO crystalline phases became stronger. However, as the deposition time increased to 60 min, the ZnO crystalline phases became weaker and the undesired KSe_2 phase appeared indicating that KCl might react with the CIS substrate at a deposition time at 60 min. The results confirm that TEA could suppress the undesired reaction between KCl and the CIS, which might cause peeling of ZnO.

4. CONCLUSION

In this research, we grew a ZnO film as a buffer layer on the ITO and the CIS substrate by ECD. Multiple material and optical analyses were performed to examine material quality of ZnO films. An appropriate amount of H_2O_2 might enhance the growth of the ZnO on the ITO substrate. Furthermore, TEA addition might suppress the reaction between KCl and the CIS substrate to enhance the growth of the ZnO film on the CIS substrate. The ZnO/CIS structure may replace the toxic CdS/CIS structure for the further development for the CIS solar cell.

REFERENCES

[1] S.J. Ahn, C.W. Kim, J.H. Yun, J. Gwak, S. Jeong, B.H. Ryu, and K.H. Yoon, J. Phys. Chem. C, 114, 8108 (2010).
[2] M. Kemell, F. Dartigues, M. Ritala, M. Leskela, Thin Solid Films, 434, 20 (2003).
[3] A. Ennaoui, M. Weber, R. Scheer, H.J. Lewerenz, Solar Energy Materials and Solar Cells, 54, 277 (1998).
[4] V. Probst, W. Stetter, W. Riedl, H. Vogt, M. Wendl, H. Calwer, S. Zweigart, K.D. Ufert, B. Freienstein, H. Cerva, F.H. Karg, Thin Solid Films, 387, 262 (2001).
[5] U. Malm, J. Malmstrfm, C. Platzer-Bjfrkman, L. Stolt,Thin Solid Films, 480, 208 (2005).
[6] J. Weng, Y. Zhang, G. Han, Y. Zhang, L. Xu, J. Xu, X. Huang, K. Chen, Thin Solid Films, 478, 25 (2005).
[7] J. Herrero, C. Guillene, Thin Solid Films, 451, 630 (2004).
[8] M. Mekhnache, A. Drici, L. Saad Hamideche, H. Benzarouk, A. Amara, L. Cattin, J.C. Bernede, M. Guerioune, Superlattices and Microstructures, 49, 510 (2011).
[9] T. Pauporte´z and D. Lincot, J. Electrochem. Soc., 148, C310 (2001).
[10]D. Lincot, Thin Solid Films, 487, 40, (2005).
[11]J. Elias, R. Tena-Zaera, and C.L. Clement, J. Phys. Chem. C, 112, 5736 (2008).
[12]H. Zhou, T. Fan, D. Zhang, Microporous and Mesoporous Materials, 100, 322 (2007).
[13]N. Orhan, M.C. Baykul, Solid-State Electronics, 78, 147 (2012).
[14]J.B. Franklin, B. Zou, P. Petrov, D.W. McComb, M.P. Ryan and M.A. McLachlan, J. Mater. Chem., 21, 8178 (2011).
[15]H. Chen, Y.M. Yeh, C.H. Liao, H.Y. Sheen, Chalcogenide Letters, 8, 703 (2011).
[16]Y.M. Yeh, H. Chen, C.H. Liao, C.B. Chen and B.Y. Chen, J. New Mat. Electrochem. Systems, 15, 103 (2012).
[17]M. Izaki and T. Omi, J. Electrochem. Soc., 144, 1949 (1997).
[18]R.E. Marottia, D.N. Guerraa, C. Bellob, G. Machadoa, E.A. Dalchiele, Solar Energy Materials & Solar Cells, 82, 85 (2004).
[19] R. Vinodkumar, K.J. Lethy, D. Beena, A.P. Detty, I. Navasa, U.V. Nayar, V.P. Pillai, V. Ganesan, V.R. Reddy, Solar Energy Materials & Solar Cells, 94, 68 (2010).