Materials Letters 89 (2012) 339–342

Contents lists available at SciVerse ScienceDirect

Materials Letters

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

Preparation of crystalline zinc oxide films by one-step electrodeposition in Reline

Mohammad Harati [a,b,1], David Love [c], Wood Ming Lau [a,b,2], Zhifeng Ding [a,*]

[a] Department of Chemistry, The University of Western Ontario, 1151 Richmond Street, London, ON, Canada N6A 5B7
[b] Surface Science Western, The University of Western Ontario, 1151 Richmond Street, London, ON, Canada N6A 5B7
[c] Rosstech Inc., 71 15th Line South, Orillia, ON, Canada L3V 6H1

ARTICLE INFO

Article history:
Received 24 June 2012
Accepted 29 August 2012
Available online 8 September 2012

Keywords:
ZnO thin films
Ionic liquid
Electrodeposition
Raman spectroscopy
X-ray photoelectron spectroscopy
Scanning electron microscopy

ABSTRACT

One-step electrodeposition of crystalline zinc oxide thin films on Molybdenum/glass substrates in a low-cost ionic liquid, Reline composed of urea and choline chloride, is presented. X-ray diffraction spectroscopy shows the thin films have wurtzite structure. Raman microspectroscopy indicates a slight oxygen deficit in the film. Both X-ray energy dispersion and X-ray photonelectron spectroscopy reveal a 1:1 stoichiometric ratio of zinc to oxygen. UV–visible absorption spectra illustrate film transparency in the wavelength range of 190–900 nm. The optimized film fabrication is attractive for applications in solar cells.

1. Introduction

We report one-step electrodeposition of ZnO in a low-cost ionic liquid, Reline that is composed of urea and choline chloride, for our patented solar cell methodology [1]. Reline is commercial name for a eutectic mixture, 1:2 M ratios, of choline chloride and urea. It is highly conductive, stable in air and water, and has a 2.5 V electrochemical window. ZnO thin films have been extensively used as n-type transparent semiconductor layer in solar cells [1–5].

They are usually fabricated using high-vacuum, high-temperature, or sol–gel processes [6–9]. Han et al. [10] reported a low-cost process for thin-film electronics. Chou and coworkers [11] fabricated ZnO nanowire/thin film structures using sputter deposition on amorphous glass substrates. Fabrication of thin films at high pressure and temperature has high capital and operational costs and it is desirable to develop inexpensive methods.

Electrochemical deposition is popular for fabrication of various materials due to the low cost, low temperature preparation condition, and environmental friendly procedure [12,13]. The first report on electrodeposition of ZnO was by Peulon and Lincot with dissolved molecular oxygen as precursor [14]. Izaki and coworkers [15] reported electrodeposition of ZnO with a wurtzit structure and 3.3 eV band gap. Pradhan and Leung [12] reported their deposition of ZnO nanopheres with diameters in 20–200 nm. Azaceta et al. [16] studied electrodeposition of ZnO in an ionic liquid, 1-butyl-1-methylpyrrolidium bis(trifluoromethane sulfony)imide.

In this report, we describe the electrochemical preparation of ZnO thin films in low-cost Reline which was used for CIGS electrodeposition by our group and Peter et al. [1,17]. Zinc perchlorate was dissolved in Reline as one of the precursors and Mo/glass substrate was employed as the substrate. The influence of the electrodeposition duration on the film morphology properties was explored.

2. Material and methods

Electrochemical set-up and characterization instruments (SEM, XRD, XPS, UV–vis, and Raman) are described elsewhere [1]. Reaction temperature was kept constant at 90.0 ± 0.1 °C by a circulating water bath (VWR, USA).

Differential pulse voltammetry (DPV) were carried out on a CHI electrochemical workstation under the following parameters: pulse amplitude of 50 mV, potential step of 10 mV, scan rate of 20 mV/s and pulse time of 200 ms. Molybdenum (Mo)/glass substrates were used as the working electrode. Two identical Pt wires were used as counter and reference electrode. The reference electrode potential was calibrated by adding ferrocenemethanol (Fc) as interim standard in Reline and all potentials will be

* Corresponding author. Tel.: +1 519 661 2111x86161; fax: +1 519 6613022.
E-mail address: zfding@uwo.ca (Z. Ding).
[1] Present address: Electrical and Computer Engineering Department, McGill University, Montreal, QC, Canada H3A 2A7.
[2] Present address: Chengdu Green Energy & Green Manufacturing Technology R&D Center, Chengdu, Sichuan 610207, China.

0167-577X/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.matlet.2012.08.136

referred to Fc^+/Fc. After deposition, the substrate was removed from the electrochemical bath, rinsed with copious distilled water, and dried under argon flow. All chemicals were purchased from Aldrich-Sigma. We prepare Reline by mixing choline chloride and urea at 70 °C on a hot plate while stirring the mixture.

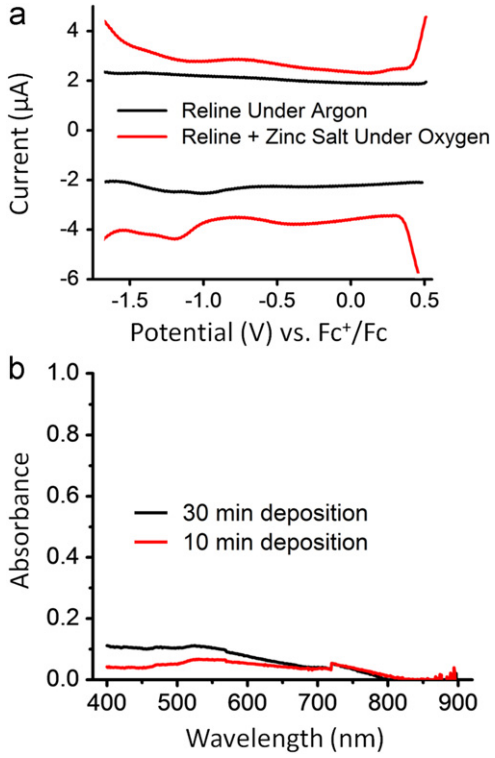

Fig. 1. (a) Differential pulse voltammograms of 5×10^{-3} M $Zn(ClO_4)_2$ solution in Reline at 90 °C, in the absence and presence of oxygen; (b) UV–vis spectra of zinc oxide thin films.

3. Results and discussion

Fig. 1a shows the electrochemical behavior of the precursor Reline solution. The DPV of Ar bubbled Reline indicates that the solvent does not exhibit significant current in the potential range of −1.700 and 0.500 V. For the oxygen bubbled zinc solution, a reduction peak was observed at −1.100 V. Similar to a previous study [16], this peak can be attributed to the reduction of dissolved oxygen to superoxide. When zinc cations are available to react with the generated superoxide ions, zinc oxide film can be formed through a peroxide route [16]. As the result, a transparent and uniform ZnO film was deposited cathodically on Mo at −1.500 V.

Two main requirements for ZnO thin films in solar cells are their transparency and low electrical resistance. With four point probes, the resistivity of ZnO films with 2 μm thickness was measured as 3.937×10^{-2} Ω m. The transparency of the film was examined using UV–vis absorption spectroscopy (Fig. 1b) and it was found that the absorbance is low and the maximal value is 6.5% and 10.1% at 530 nm for 10 min and 30 min deposited films, respectively. The absorbance shows approximately a linear decrease with the increase of wavelength, which may be caused by scattering of the special wurtzite structure [18].

The chemical compositions of ZnO films were investigated by XPS. Fig. 2a demonstrates the symmetrical O 1s spectrum with a peak centered at 532.85 eV, a typical value attributed to the oxygen [19]. Fig. 2a also shows a typical Zn 2p spectrum in a ZnO crystalline thin film with peak positions of typical bulk ZnO nanostructures. The Raman spectrum of the ZnO thin film in Fig. 2b demonstrates bands as following: 101 cm^{-1} (E2), 361 cm^{-1}, 383 cm^{-1} (A1 TO), 407 cm^{-1} (E1 TO), 446 cm^{-1} (E2), 594 cm^{-1} (E1 LO) [20,21]. The peak at 537 cm^{-1} indicates slight oxygen deficiency in the film [20]. However, according to results reported by Mcguire [21]and Xu et al. [20] peaks at 221 cm^{-1} and 556 cm^{-1} are related to oxygen deficiency which are absent in our spectrum. The peak at 446 cm^{-1} is attributed to high-frequency vibration modes of E2, which corresponds to a band characteristic of the wurtzite phase. The peak 318 cm^{-1} has been assigned as second order modes [20,21].

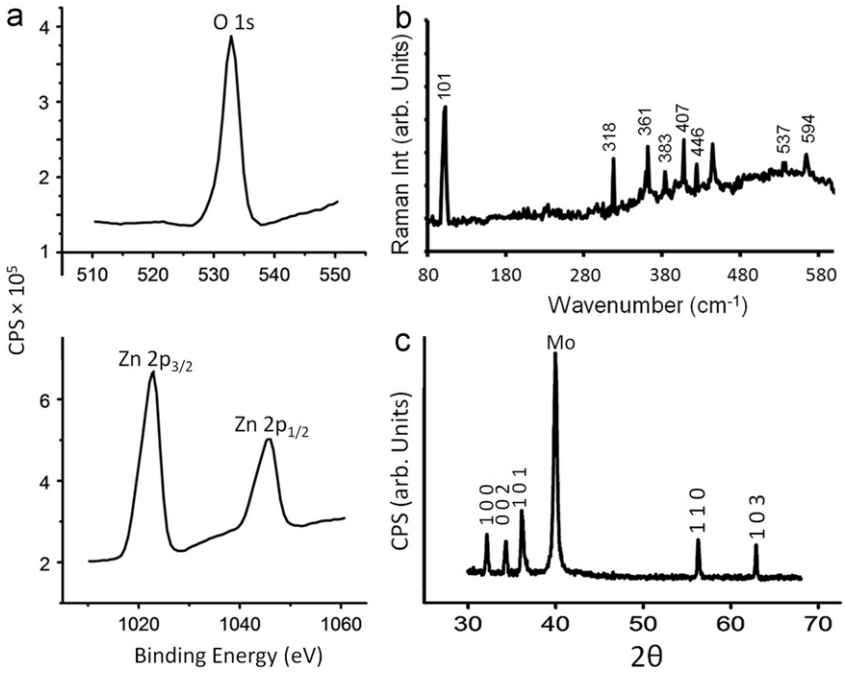

Fig. 2. (a) XPS spectra of a ZnO thin film O 1s (up) and Zn 2p (down). (b) Raman spectrum of an as-deposited zinc oxide thin film. (c) XRD patterns of a typical electrodeposited ZnO film.

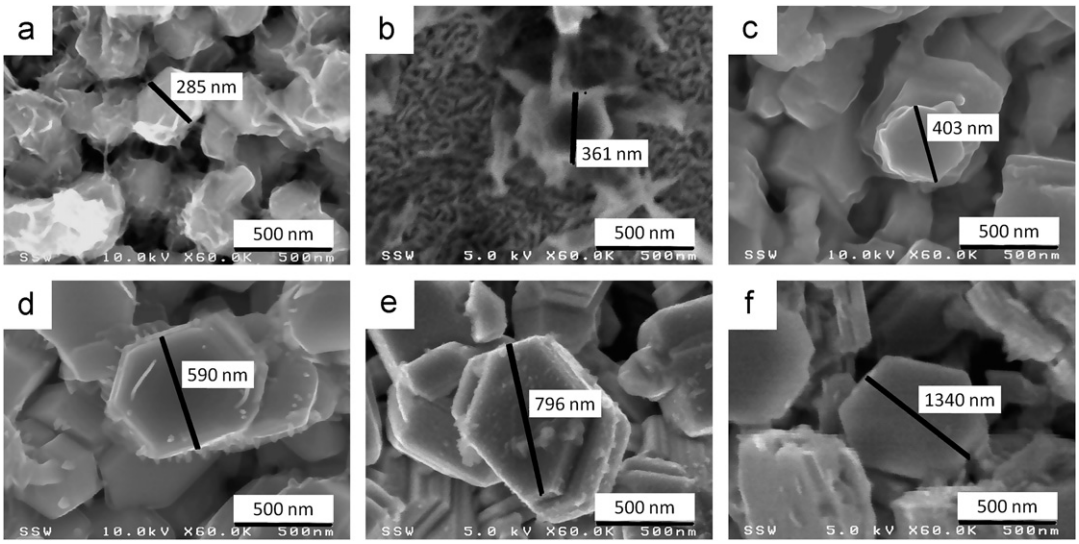

Fig. 3. SEM images of zinc oxide films with different deposition time: (a) 10 min, (b) 20 min, (c) 30 min, (d) 60 min, (e) 90 min, and (f) 120 min.

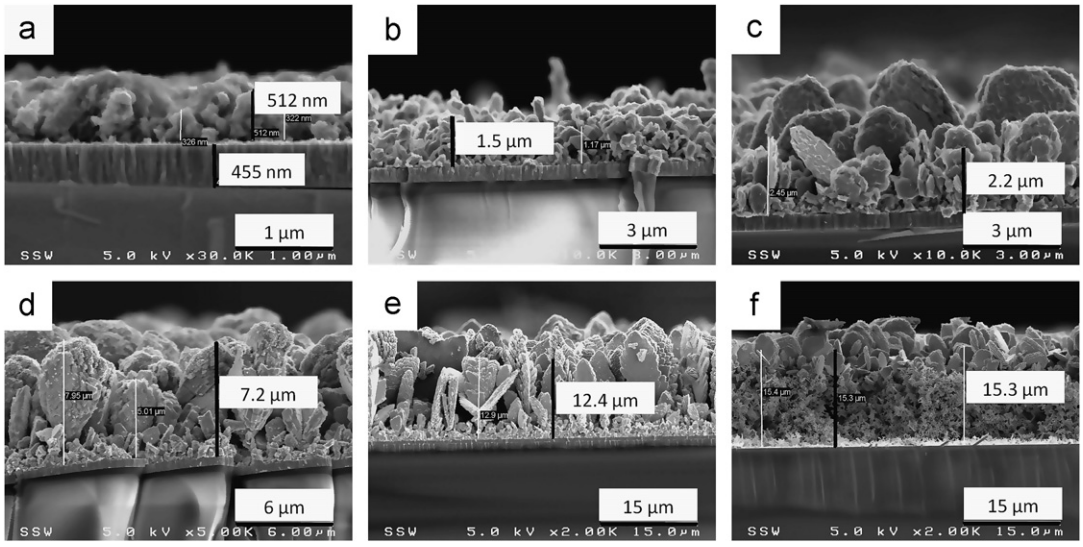

Fig. 4. Cross-section SEM images of zinc oxide films with different deposition time: (a) 10 min, (b) 20 min, (c) 30 min, (d) 60 min, (e) 90 min, and (f) 120 min.

The XPS data together with Raman spectroscopy unambiguously illustrate the formation of ZnO on Mo/glass substrate.

Fig. 2c shows a typical XRD spectrum of the ZnO crystalline thin films deposited at potential of −1.500 V. All observed peaks can be indexed to either ZnO or molybdenum. Sharp peaks appear at $2\theta = 32.2^\circ$, 34.4°, 36.2°, 56.4°, and 62.9° can be indexed by the (100), (002), (101), (110), and (103) reflections of the hexagonal wurtzite structure of ZnO, respectively [18,20,22]. This confirms that crystalline ZnO was obtained electrochemically at a temperature of 90 °C which agrees with Raman spectra. EDX, and XPS results showed that zinc is slightly higher than oxygen in the thin film.

The influence of the deposition duration on the morphology of ZnO thin films was examined by scanning electron microscope (SEM) and is demonstrated in Fig. 3. As can be inferred from SEM, the zinc oxide thin films are hexagonal prisms. The thickness of the thin films is measured using cross-section SEM technique (Fig. 4). The thickness changes from 300 nm to more than 15 µm for deposition duration of 10 min and 120 min, respectively. We calculated the growth rate from the film thicknesses observed on the cross-section SEM images (Fig. 4). Under the studied conditions, the growth rate is higher than that using different medium or method for deposition [13]. Rousset and coworkers calculated the film growth kinetics from film thickness observed by cross-section SEM to be 0.6 µm h^{-1} in perchlorate electrolyte and 2.5 µm h^{-1} in the nitrate solution [13]. According to our growth rate measurements, it also depends on deposition duration, as it starts with 2.32 µm h^{-1} for 10 min deposition and gradually increases to as high as 11.40 µm h^{-1} for 90 min deposition. Cross-sectional SEM images (Fig. 4) shows that electrodeposits are polycrystalline films. These films were regularly continuous, and no holes were visible. The chemical composition of the thin films was determined using EDX, which reveals that the thin films are composed of Zn and O, and quantitative analysis indicates that the atomic ratio of Zn to O is about their stoichiometric ratio. Electrodeposition was carried out at lower temperatures and EDX results showed that films are non-stoichiometric and as the deposition temperature lowers, the films tend to be more metallic.

In summary, electrodeposition of ZnO films in Reline was realised, for the first time, for applications in thin film solar cells. Absorption spectrum confirmed the transparency in wavelength range of 400–900 nm. EDX, XPS, Raman, and XRD results indicated that the ZnO films have wurtzite structure with 1:1 stoichiometric

ratio of zinc to oxygen. Our method has high ZnO deposition rate between 2.3 $\mu m\,h^{-1}$ and 11 $\mu m\,h^{-1}$, depending on deposition duration. Other advantages of our one-step electrodeposition method using Reline are low cost and great solubility for commercial available zinc salts.

Acknowledgments

We acknowledge financial support from Rosstech Inc., OCE, NSERCl, CFI/OIT, PREA and UWO, and the quality service from our Electronic Shop and ChemBio Store. W.M. Lau thanks the support from funding agencies to his research in China.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.matlet.2012.08.136.

References

[1] Harati M, Jia J, Giffard K, Pellarin K, Hewson C, Love DA, Lau WM, Ding Z. Phys Chem Chem Phys 2010;12:15282–90.
[2] Vasekar PS, Jahagirdar AH, Dhere NG. Thin Solid Films 2010;518:1788–90.
[3] Tao K, Zhang D, Wang L, Zhao J, Cai H, Sui Y, Qiao Z, He Q, Zhang Y, Sun Y. Sol Energy Mater Sol Cells 2010;94:709–14.
[4] Kaplan R, Kaplan B, Hegedus SS. Solid-State Electron 2010;54:22–7.
[5] Grimm A, Klenk R, Klaer J, Lauermann I, Meeder A, Voigt S, Neisser A. Thin Solid Films 2009;518:1157–9.
[6] Anas S, Mangalaraja RV, Ananthakumar SJ. Hazard Mater 2010;175:889–95.
[7] Zhang Y, Xiang Q, Xu J, Xu P, Pan Q, Li FJ. Mater Chem 2009;19:4701–6.
[8] Maldonado A, Tirado-Guerra S, Cãzares JM, Olvera Mde la L. Thin Solid Films 2010;518:1815–20.
[9] Nian H, Hahn SH, Koo KK, Kim JS, Kim S, Shin EW, Kim EJ. Mater Lett 2010;64:157–60.
[10] Han SY, Chang CH, Lee DH, Herman GSJ. Disp Technol 2009;5:520–4.
[11] Chou TL, Wu WY, Ting JM. Thin Solid Films 2009;518:1553–6.
[12] Pradhan D, Leung KT. Langmuir 2008;24:9707–16.
[13] Rousset J, Saucedo E, Lincot D. Chem Mater 2009;21:534–40.
[14] Peulon S, Lincot D. Adv Mater 1996;8:166–70.
[15] Izaki M, Omi T. Appl Phys Lett 1996;68:2439–40.
[16] Azaceta E, Tena-Zaera R, Marcilla R, Fantini S, Echeberria J, Pomposo JA, Grande H, Mecerreyes D. Electrochem Commun 2009;11:2184–6.
[17] Shivagan DD, Dale PJ, Samantilleke AP, Peter LM. Thin Solid Films 2007;515:5899–903.
[18] Liu Z, Jin Z, Li W, Liu X, Qiu J, Wu W. Mater Lett 2006;60:810–4.
[19] Zhang R, Fan L, Fang Y, Yang SJ. Mater Chem 2008;18:4964–70.
[20] Xu XL, Lau SP, Chen JS, Chen GY, Tay BK. J Cryst Growth 2001;223:201–5.
[21] McGuire K, Pan ZW, Wang ZL, Milkie D, Menendez J, Rao AM. J Nanosci Nanotechnol 2002;2:499–502.
[22] Chatman S, Poduska KM. ACS Appl Mater Interfaces 2009;1:552–8.