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Low temperature cathodic electrodeposition of nanocrystalline zinc oxide thin films

Lisha Zhang [a,b], Zhigang Chen [a,c], Yiwen Tang [a,*], Zhijie Jia [a]

[a] *Institute of Nano-science and technology, Central China Normal University, Wuhan 430079, China*
[b] *Department of Environmental Engineering, Shanghai Second Polytechnic University, Shanghai 201209, China*
[c] *Institute of Advanced Materials, Fudan University, Shanghai 200433, China*

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Abstract

This paper investigates electrochemical behavior of ZnO thin films deposition on transparent conducting optically glass from a simple aqueous zinc nitrate solution. At low temperature, ZnO films with grain sizes between 10 and 15 nm are obtained by controlling growth rate. The X-ray diffraction pattern shows that ZnO film has a hexagonal wurtzite structure and the preferred growth orientation is the (002) direction. Detailed X-ray photoelectron spectroscopy analysis indicates the presence of metallic Zn, OH and H_2O species in the as prepared ZnO films. In addition, ZnO thin film changes from Zn-rich to O-rich after being annealed in air. Optical characterizations show that the films as prepared and annealed at 250 °C have high optical transmittance (>90%) in the visible wavelength range and the band gap of the nanocrystalline ZnO films is 3.37 eV.

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1. Introduction

Thin films of zinc oxide (ZnO) have been object of quickly growing attention in the last few years because of its interesting properties such as resistivity control over the range 10^{-3} to 10^{5} Ωcm, transparency in the visible wavelength, high electrochemical stability, direct band gap, abundance in nature, and absence of toxicity [1,2]. They are widely used in a variety of industrial and technical application in piezo-electric films in surface acoustic wave devices [3], chemical sensors [4], catalysis [5] and photovoltaics as an n-type window layer [6].

ZnO thin films have been prepared by a wide variety of techniques such as pulsed laser deposition [7], sputtering [8], and electrodeposition [9–13]. In particular, the electrodeposition method has advantages over other processes because of its simplicity, low equipment cost and the possibility in making large area thin films. For example, Pauporte and Lincot have reported the heteroepitaxial electrodeposition of zinc oxide films on GaN [12]. Gal et al. have electrodeposited ZnO on $Cu(In,Ga)Se_2$ as a buffer layer [13]. However, the grain of such ZnO electrodeposited from aqueous solution is micron-sized. Recently the use of nanostructured substrates has been proposed as a way to improve the device performance in light-collecting devices such as solar cells. The design of nanostructured surfaces coated with extremely thin-absorber should lead to minimize the optical losses and to enhance the carrier transfer from the active region to the contacts [14,15]. Though nanocrystalline ZnO films can be obtained by electrodeposition from non-aqueous solution, this means is high cost, not simple and not suitable for some applications [16]. In this paper, we investigate electrochemical behavior of ZnO thin films deposition from a simple aqueous zinc nitrate solution, design to electrodeposit nanostructured ZnO film and present the results of structural, morpholog-

* Corresponding author. Tel.: +86 27 67861185; fax: +86 27 67861185.
E-mail address: ywtang@phy.ccnu.edu.cn (Y. Tang).

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ical and optical studies of nanocrystalline ZnO thin films electrodeposited onto transparent conducting optically (TCO) glass.

2. Experimental details

A conventional three electrodes cell was used with TCO glass (fluorine-doped SnO_2 coated glass, sheet resistance is about 10–15 Ω/□) substrate as the working electrode, platinum as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode to electrodeposit ZnO films. All the potentials are reported versus the potential of SCE. The electrolyte consisted of 0.01~0.1 M $Zn(NO_3)_2$ and 0.1 M KNO_3 solution with an initial pH adjusted to 5.0±0.1[1]. Analytical grade reagents were used. The bath temperature was controlled between 0 and 80 °C by a DkB-501A high precision water bath and the electrolyte was stirred continuously using a magnetic stirrer. Prior to the film deposition, the TCO substrates were cleaned with detergent and diluted hydrochloric acid and were then rinsed with distilled water. Electrodeposition was carried out under potentiostatic condition using Princeton Applied Research Model 263 A Potentiostat/Galvanostat.

The samples were annealed in air at different temperatures for 30 min. The surface morphology of the films was studied by JSM-6700F scanning electron microscope (SEM) operated at an accelerating voltage of 8 kV. X-ray diffraction (XRD) measurements were performed by a Philips MRD diffractometer with Cu Kα radiation. X-ray photoelectron spectroscopy (XPS) measurements were performed using a Kratos XSAM 800 spectrometer having a Mg Kα (1253.6 eV) X-ray source, with power given by the emission of 16 mA at a voltage of 12 kV. The usual pressure in the sample analysis chamber was about 10^{-8} Pa. Argon ion flux was employed to sputter the surface, with energy of 4 keV, emission of 10 mA, incidence angle of 45°, during 10 min. The spectra were recorded in the fixed-retardation-ratio mode. Recorded spectra were calibrated in binding energy according to C 1 s at 284.8 eV. Optical absorption studies were carried out employing a Shimadzu UV-2550 ultraviolet-visible-near infrared spectrophotometer.

3. Results and discussion

The cathodic electrodeposition of ZnO thin films from nitrate solution is thought to proceed via the reduction of nitrate ions according to the Eq. (1). The electrochemically generated hydroxide ions then react chemically with Zn^{2+} ions in the solution to form $Zn(OH)_2$ at the cathode. Subsequently, $Zn(OH)_2$ is spontaneously dehydrated into ZnO. (Eq.(2)) [10,17].

$$NO_3^- + H_2O + 2e^- \rightarrow NO_2^- + 2OH^- \quad (1)$$

$$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2 \rightarrow ZnO + H_2O \quad (2)$$

The overall expression of the reaction therefore is,

$$Zn^{2+} + NO_3^- + 2e^- \rightarrow ZnO + NO_2^- \quad (3)$$

The linear sweep voltammogram of ZnO films deposition from $Zn(NO_3)_2$ and KNO_3 solution at different bath temperatures is shown in Fig. 1. The sweep is scanned cathodically at 10 mV/s. With the decrease of Zn^{2+} ions concentration from 0.1 to 0 M, the cathodic currents drop significantly at the same potential as shown in Fig. 1 (c), (d) and (e), although the concentration of NO_3^- in sweep (e) is higher than that in sweep (d). This phenomenon may be due to the catalytic role of Zn^{2+} ions to the reduction of nitrate [17]. Furthermore, Fig. 1 (a), (b) and (d) show that with the decrease of bath temperature, the onset potential for the reduction negatively shifts and the cathodic currents drop significantly at the same potential. Since the grain of ZnO electrodeposited at high bath temperature is micron-sized as a result of the high growth rate of ZnO [10,16,17], the nanocrystalline ZnO films may be prepared by controlling growth rate at low temperature. In our work, therefore, electrodeposition of ZnO film is carried out in the solution of 0.01 M $Zn(NO_3)_2$ and 0.1 M KNO_3 at bath temperature of 0 °C. In addition, we also find that it is difficult to electrodeposit ZnO thin film at the electrode potential higher than −1.28 V at 0 °C because of too low growth rate. Electrodeposition at electrode potential lower than −1.35 V leads to too high cathodic current, even produces H_2 gas at the cathode surface and results in the reduction of plenty of Zn^{2+} ions to metallic Zn. In order to obtain suitable growth rate and to avoid hydrogen evolution and metallic Zn formation, the electrode potential is held at −1.30 V.

ZnO thin films are electrodeposited for 1 h in the solution of 0.01 M $Zn(NO_3)_2$ and 0.1 M KNO_3 at bath

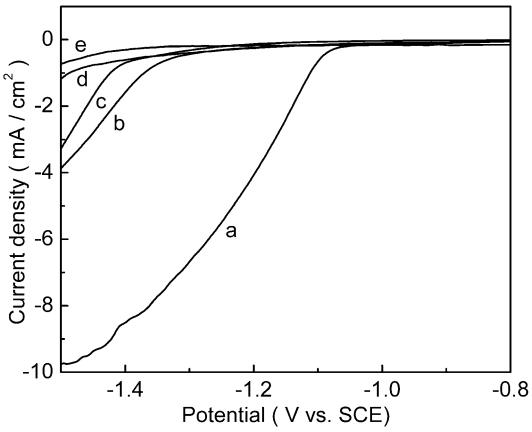

Fig. 1. Linear sweep voltammogram of ZnO deposition from aqueous mixed solutions of $Zn(NO_3)_2$ and KNO_3, where (a), (b) and (d) is respectively corresponding to 0.01 M $Zn(NO_3)_2$ and 0.1 M KNO_3 at bath temperature of 75, 30 and 0 °C, (c) is corresponding to 0.1 M $Zn(NO_3)_2$ and 0.1 M KNO_3 at 0 °C, and (e) is corresponding to 0.2 M KNO_3 at 0 °C. Sweep rate=10 mV/s.