

Invited paper

Thin-film transistors with active layers of zinc oxide (ZnO) fabricated by low-temperature chemical bath method

Hua-Chi Cheng^{a,b,*}, Chia-Fu Chen^a, Cheng-Chung Lee^b^a Department of Materials Science and Engineering, National Chiao Tung University, Taiwan, R.O.C.^b Electrics Research and Service Organization, Industrial Technology Research Institute, Taiwan, R.O.C.

Available online 19 August 2005

Abstract

Thin-film transistors (TFTs) with active channel layers of zinc oxide (ZnO) using a low-temperature chemical bath deposition have been studied. The ZnO films were fabricated on the defined-areas of bottom-gate type TFTs plate by immersing in a chemical bath containing zinc nitrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and dimethylamineborane (DMAB) aqueous solution at 60 °C. Silicon oxide (SiO_2) was used as the gate insulator. Produced TFTs plate was dried in the air at 100 °C, specially, without any further annealing. Current–voltage (I – V) properties measured through the gate infer that the ZnO channel is n-type. Devices were achieved that $I_{\text{on}}/I_{\text{off}}$ ratio was more than 10^5 , for which the channel mobility on the order of $0.248 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ has been determined.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Chemical bath method; Zinc oxide; Thin-film transistors; Active channel layers

1. Introduction

Zinc oxide (ZnO), a transparent film, is very popularly used due to its unique optical and electronic properties in solar cells [1], photo detectors [2], light emitting devices [3], gas sensor elements [4], and surface acoustic wave guides [5]. Also, ZnO films have recently been studied as the active channel material in thin-film transistors development because of its exhibiting n-type semiconductive characteristic with wide band gap of 3.3 eV, excellent chemical and thermal stability, and can be well-oriented crystalline on various substrate [6–8]. Especially, the Hall effect mobility measured at room temperature for single crystals is on order of $200 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [9].

Several methods are applied to prepare ZnO films, both physical and chemical deposition technologies including sputtering [10], pulsed laser deposition [11], chemical vapor deposition (CVD) [12], molecular beam epitaxy [13], and

sol–gel process [14] etc. However, most of the methods were not well suited for large area coating, low-temperature processing, and low process cost. So far, the abovementioned methods could not be used for ZnO crystal fabrication below 150 °C. Again, the equipment is expensive for large area process. Therefore, chemical bath deposition (CBD) has been an attractive technology which is simple and low cost for thin-film fabrication. There are many previous articles discussing the ZnO films using electroless deposition in solution bath and indicating the feasibility of low temperature [15–19]. Preparation of oxide film in a chemical solution bath presents several advantages: (i) films can be obtained on substrates at low temperature, below 100 °C, (ii) the thickness and morphology of film can be controlled by deposition parameters, (iii) the equipment is relatively cheap, and (iv) the technique is more environmentally friendly. These supply the technique compatibility for the low-cost process and good quality.

In the present article, we decided the patterning method of ZnO film and performed the bottom-gate type TFT device with a patterned active channel ZnO film on that used CBD method. Also, the properties of films and characteristics of ZnO-TFT were studied.

* Corresponding author. Electrics Research and Service Organization, Industrial Technology Research Institute, Taiwan, R.O.C. Tel.: +886 3 5917731; fax: +886 3 5826842.

E-mail address: Hua-Chi-Cheng@itri.org.tw (H.-C. Cheng).

2. Experimental details

2.1. Film deposition procedure

The TFTs had a simple bottom-gate device configuration on a Corning 1737 glass substrate (Fig. 1. insert), where underlying ITO, 100 nm thick, was used as the gate electrode, selecting a silicon oxide (SiO_2) film for the gate dielectric with thickness of 300 nm, and ITO film thickness of 100 nm as the source and drain electrodes. The TFT was defined as a channel width $W=500\ \mu\text{m}$ and channel length $L=10\ \mu\text{m}$. The active channel region was fabricated using standard lithography process. First, the photo resist was coated and developed to pattern the active channel region. Then the ZnO film was following processed by CBD technique. Last, the photo resist was stripped and the TFT was yield (the cross-sectional and top view of the ZnO-based thin-film transistor was showed on Fig. 1(a), (b)).

CBD was carried out in a beaker with a soak aqueous solution containing 0.1 mol/L zinc nitrate and 0.03 mol/L dimethylamineborane placed upon a heater–stirrer during the growth process at temperatures $60\ ^\circ\text{C}$. Prior to deposition, the glass substrate was activated by an industrially employed two-step Pd/Sn process using sensitizer (SnCl_2 , 1 g/L; 32% HCl, 1 ml/L) and activator (PdCl_2 , 0.1 g/L; 32% HCl, 0.1 mol/L) [20,21], then immersed the substrate in the soak solution for 30 min. The thickness of the ZnO film could be controlled by tuning the soak concentration or immersing time. Finally, the substrate was rinsed with DI water and dried with nitrogen gas then baked on hot-plate at $100\ ^\circ\text{C}$ for 5 min.

2.2. Characterization techniques

The deposited crystal structure was identified by X-ray diffractometry (XRD) (Mac Science M18XHF-SRA) using

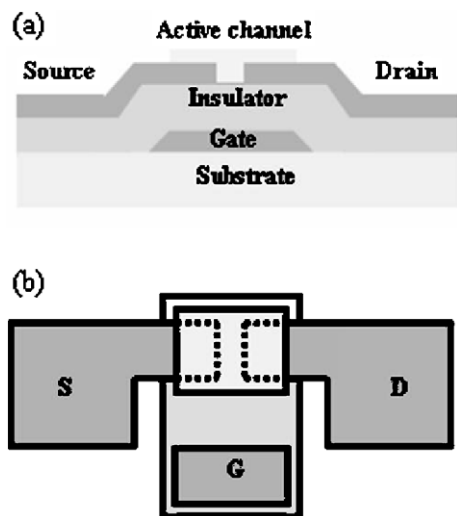


Fig. 1. Schematic (a) cross-sectional and (b) top view of the ZnO-based thin-film transistor.

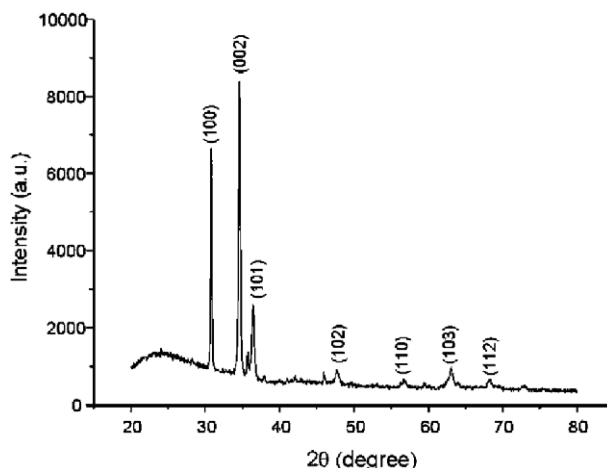


Fig. 2. X-ray diffraction spectrum of the ZnO thin film on SiO_2 surface prepared by the CBD.

a conventional 2θ scans over a range from 15° to 80° operated at 50 kV and 200 mA, the morphology was characterized by scanning electron microscopy (SEM; LEO 1530). The transistors were analyzed with an Agilent 4155B semiconductor parameter analyzer. The samples were measured in the dark.

3. Results and discussions

The crystallographic structure of the films has been studied by X-ray diffraction. Fig. 2 shows the XRD spectrum of ZnO film which was deposited on the SiO_2 surface of a TFT device by soaking in the aqueous solution with 0.1 mol/L zinc nitrate and 0.03 mol/L DMAB. The diffraction peaks (100), (002), and (101) indicate that the produced ZnO crystals are wurtzite structure, and the morphologies consist of hexagonal column. In addition, mainly peak (002) indicates preferential c -orientation of the crystals [22], in other words, that grains are mainly grown with c -axis vertical to the substrate. Moreover, from the recorded spectra (Fig. 2), the minor diffraction peaks of (102), (110), (103), and (112) are approved of randomly oriented of the ZnO film [23]. The regular direction growth can be explained as follows: for the electroless deposition, the crystalline morphology was led by nucleation and growth conditions. The primary crystal growth of ZnO could be enhanced by means of $\text{SnCl}_2/\text{PdCl}_2$ two-step surface pretreatment. According to the present paper of M. Charbonnier and M. Romand [24], proposed Sn (+2) ions adsorb on oxygenated groups of substrate through the formation of Sn–O covalent bonds using SnCl_2 solutions, i.e., through the sharing of their valence electrons. Then Pd^{+2} ions attach on tin species via chemical adsorption. The primary ZnO crystallite would grow on the Pd catalyst sites by means of heterogeneous nucleation [3].

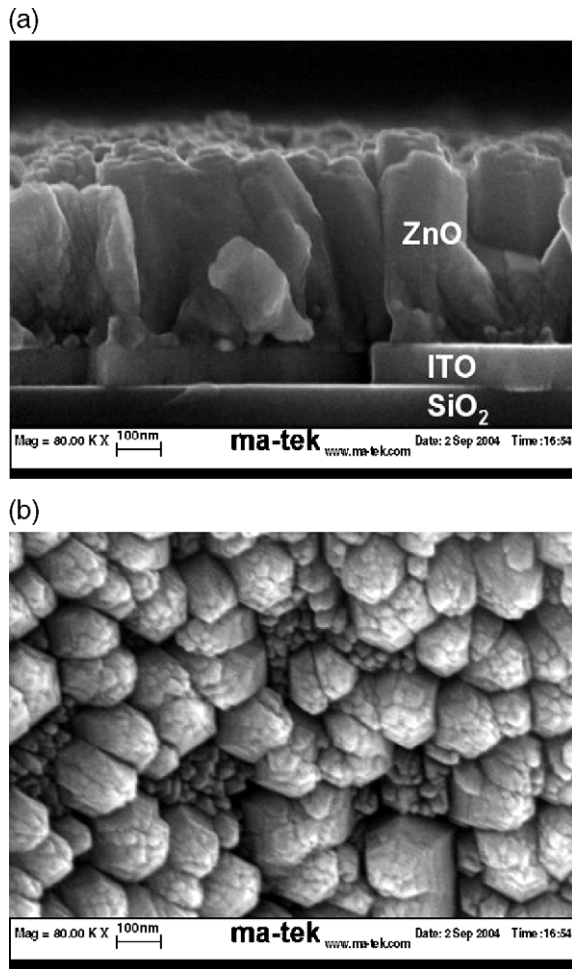


Fig. 3. SEM images of ZnO film deposited at 60 °C from 0.1 mol/L zinc nitrate and 0.03 mol/L dimethylamineborane solution. (a) Cross-sectional morphology, (b) plane-view morphology.

Fig. 3(a) and (b) show the image of local ZnO film on TFT device by SEM, which are, respectively, cross-sectional and plane-view morphology. Hexagonal rods are observed which correspond to the basal plane of the hexagons (Fig. 3(a)). The ZnO film is formed of regular arrangement and compact amassment rods vertical to the substrate and the mean thickness is 400 nm. As Fig. 3(b) shows, the crystals are closely packed, however, the composition of columns have clear and dull interface at the same time. We define the grains which are formed with many small columns and possess clear interface with each other. The grain size is from several tens to 200 nm. For TFT application, the active channel layer with larger grain size and less grain boundary can conduce to the electron mobility.

Fig. 4(a) and (b) show the electrical characteristics of the ZnO-TFT in which the active channel layer ZnO was fabricated by CBD method without any annealing. Current–voltage (I – V) properties measured through the gate infer that the ZnO channel is n-type. Because some drain current can still be measured at 0 V of gate voltage

(inset Fig. 4(a)), the device is a depletion-mode TFT. As shown in Fig. 4(b), the I_d – V_g curve, there is current leakage in the beginning due to the electrons trap at the grain boundaries that fill as the gate is charged. Again, the electric field will induce the breakdown too. While the traps filled out gradually, the I_d decreased. With the gate voltage increasing, the TFT device will induce channel then current increase. The phenomenon also appeared in TFT of other semiconductor materials and details were discussed [25–28].

The I_{on}/I_{off} ratio was measured higher than 10^5 . The field effect mobility (μ_{FE}) and threshold voltage (V_{th}) could be calculated by fitting the constant slope line to the plots of

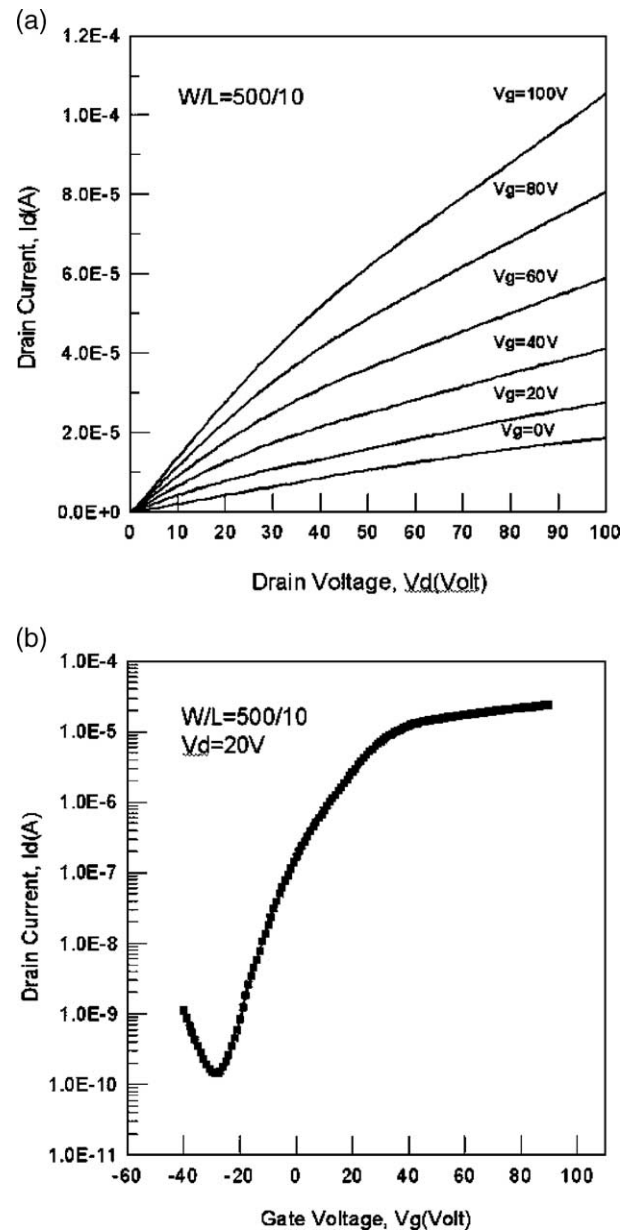


Fig. 4. Electrical characteristics of the ZnO-TFT which the active channel layer ZnO was fabricated by CBD method. (a) I_d – V_d curve, (b) I_d – V_g curve.

the square root of drain current vs. gate voltage. The drain current in the saturated regions is calculated by the following equation,

$$I_{\text{d,sat}} = \mu_{\text{FEsat}} (W/2L) C_1 (V_{\text{gs}} - V_{\text{th}})^2$$

where W and L are the channel width and length respectively, C_1 is the capacitance per unit area of gate insulator. The saturated regions mobility (μ_{FEsat}) was calculated of $0.248 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.

4. Conclusion

A ZnO film using active channel layer of ZnO-TFT was fabricated by CBD in a aqueous solution containing zinc nitrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and dimethylamineborane (DMAB) aqueous solution at 60°C . The grains of the ZnO films are mainly grown with c -axis vertical to the substrate due to high participate of (002), also the ZnO crystals are hexagons (wurtzite structure). According to the present study, the TFT device was successful made, it was depletion-mode and the $I_{\text{on}}/I_{\text{off}}$ ratio achieved was more than 10^5 , the channel mobility on the order of $0.248 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ had been determined.

References

- [1] K. Keis, E. Magnusson, H. Lindstorm, S.E. Lindquist, A. Hagfeldt, Sol. Energy 73 (2002) 51.
- [2] S. Liang, H. Sheng, Y. Liu, Z. Hio, Y. Lu, H. Shen, J. Cryst. Growth 225 (2001) 110.
- [3] N. Saito, H. Haneda, T. Sekiguchi, N. Ohashi, I. Sakaguchi, K. Koumoto, Adv. Mater. 14 (2002) 418.
- [4] Pizzini, N. Butta, D. Narducci, M. Palladino, J. Electrochem. Soc. 136 (1989) 1945.
- [5] F.C.M. Van de Pol, Ceram. Bull. 69 (1990) 1959.
- [6] S. Masuda, K. Kitamura, Y. Okumura, S. Miyatake, H. Tabata, T. Kawai, J. Appl. Phys. 93 (2003) 3.
- [7] Y. Kwon, Y. Li, Y.W. Heo, M. Jones, P.H. Holloway, D.P. Norton, Z.V. Park, S. Li, Appl. Phys. Lett. 84 (2004) 14.
- [8] B.J. Norris, J. Anderson, J.F. Wager, D.A. Keszler, Appl. Phys. 36 (2003) L105.
- [9] S. Arulkumaran, et al., Appl. Phys. Lett. 81 (2002) 1131.
- [10] Y.E. Yee, J.B. Lee, Y.J. Kim, H.K. Yang, J.C. Park, H.J. Kim, J. Vac. Sci. Technol., A 14 (1996) 1943.
- [11] V. Craciun, J. Elders, J.G.E. Gardenievs, I.W. Boyd, Appl. Phys. Lett. 65 (1994) 2963.
- [12] Y. Natsume, H. Sakata, T. Hirayama, Phys. Status Solidi, A 148 (1995) 485.
- [13] K. Ogata, K. Sakurai, Sz. Fujita, Sg. Fujita, K. Matsushige, J. Cryst. Growth 214 (2000) 312.
- [14] Y. Natsume, H. Sakata, Thin Solid Films 372 (2000) 30.
- [15] M. Izaki, T. Ohmi, Appl. Phys. Lett. 68 (1996) 166.
- [16] M. Izaki, J. Katayama, J. Electrochem. Soc. 147 (2000) 210.
- [17] K. Ito, K. Nakamura, Thin Solid Films 286 (1996) 35.
- [18] P. O'Brien, T. Saeed, J. Knowlcs, J. Mater. Chem. 6 (1996) 1135.
- [19] S. Yamabi, H. Imai, J. Mater. Chem. 12 (2002) 3773.
- [20] L.G. Svendsen, T. Osaka, H. Sawai, J. Electrochem. Soc. 130 (2000) 2252.
- [21] C.H. de Minjer, P.F.J.v.d. Boom, J. Electrochem. Soc. 120 (1997) 1644.
- [22] International Centre for Diffraction Datas, Joint Committee on Powder Diffraction Standards, Swarthmore, PA, 1986, Card 36-1451.
- [23] M. Izaki, J. Electrochem. Soc. 146 (1999) 4517.
- [24] M. Charbonnier, M. Romand, Adhes. Adhes. 23 (2003) 277.
- [25] J.S. Meth, S.G. Zane, K.G. Sharp, S. Agrawal, Thin Solid Films 444 (2003) 227.
- [26] P.F. Carcia, R.S. McLean, M.H. Reilly, G. Nunes Jr., Appl. Phys. Lett. 80 (2003) 7.
- [27] J. Nishii, F.M. Hossain, S. Takagi, T. Aita, K. Saikusa, Y. Ohman, I. Ohkubo, S. Kishimono, A. Ohtomo, T. Fukumura, F. Matsukura, Y. Ohno, H. Koinuma, H. Ohno, M. Kawasaki, Jpn. J. Appl. Phys. 42 (2003) L 347.
- [28] William S. Wong, Steven E. Ready, Jeng-Ping Lu, Robert A. Street, IEEE Electron Device Lett. 24 (2003) 9.