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Effect of preheating temperature on structural and optical properties of ZnO thin films by sol–gel process

Young-Sung Kim [a,*], Weon-Pil Tai [b], Su-Jeong Shu [a]

[a] Advanced Material Process of Information Technology, Sungkyunkwan University, Suwon 440-746, South Korea
[b] Institute of Advanced Materials, Inha University, Inchon 402-751, South Korea

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Abstract

ZnO thin films are prepared on glass substrate by sol–gel spin-coating method and the effect of preheating temperature on *c*-axis preferred orientation and optical properties of the films are investigated. The ZnO thin film that was preheated at 275 °C and post-heated at 650 °C using a sol with Zn concentration of 0.7 mol/l is highly oriented along the (002) plane. The transmittances of ZnO thin films preheated at 200~300 °C and post-heated at 650 °C are over 85% in visible range and exhibit absorption edges at about 368 nm. The optical band gap energy is evaluated to be 3.24~3.26 eV. The photoluminescence shows the ultraviolet emission at near band edge and broad green-yellow radiation at 490~620 nm. The effect of preheating temperature on structural and optical properties of ZnO thin films is discussed.

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Keywords: Zinc oxide; Sol–gel process; Optical properties; Photoluminescence

1. Introduction

Recently, ZnO thin films have been studied extensively due to their potential applications, as transparent electrodes in display, metal oxide semiconductors in optoelectronic devices, and piezoelectric devices. ZnO is a II–VI group compound semiconductor with a wide band gap. ZnO has a hexagonal wurtzite structure ($c=0.521$ nm, $a=0.325$ nm) [1] with oxygen atoms on hexagonal sites and zinc atoms on tetrahedral sites. In particular, it has been demonstrated that zinc oxide film with preferential orientation along the *c*-axis operates as surface acoustic wave devices because of their large piezoelectric constant [2,3]. ZnO thin films can be used in the fabrication of hydrogenated amorphous silicon solar cells owing to their better stability in hydrogen plasma than that of indium tin oxide [4]. Besides, ZnO thin films can find applications in gas sensor, varistor, and light emission display [5].

ZnO thin films have been prepared by various film deposition methods, such as sputtering [6], pulsed laser deposition [7], chemical vapor deposition [8], spray pyrolysis [9,10], and sol–gel process [11,12]. Although physical deposition methods have been extensively used, sol–gel process has distinct advantages over the other techniques due to excellent compositional control, homogeneity on the molecular level due to the mixing of liquid precursors, and lower crystallization temperature.

The preferential orientation and photoluminescence of the ZnO thin films prepared by the sol–gel process have been reported. In some work, the preferred crystal growth does not occur by using isopropanol as a solvent which has a low boiling temperature because its not enough to structurally be relaxed. However, the crystal orientation can be controlled by lowering heat treatment temperature [13,14]. Furthermore, in two sol solvents, 2-methoxyethanol–monoethanolamine (MEA) and isopropanol– diethanolamine, the former has a highly preferred orientation along the (002) plane, the latter has no *c*-axis growth tendency. Many studies to control preferential orientation have concentrated

* Corresponding author. Tel.: +82 31 299 6702; fax: +82 31 290 5644.
E-mail address: youngsk@skku.edu (Y.-S. Kim).

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on post-heating treatment. However, studies on preheating temperature have rarely been carried out.

In this study, a solvent of low boiling temperature, isopropanol, is used to promote a crystal orientation along the (002) plane and optical properties. ZnO thin films from zinc acetate dihydrate–isopropanol–MEA solution were deposited on glass substrates by the spin-coating method. The tendency of *c*-axis growth of ZnO thin films is investigated as a function of preheating temperature. The crystal orientation, structural and optical properties are performed by X-ray diffraction (XRD), scanning electron microscope (SEM), X-ray photoelectron spectroscopy (XPS), ultraviolet (UV)–visible spectrometer and photoluminescence (PL) spectrofluorometer.

2. Experimental procedure

Zinc acetate dihydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$) was first dissolved in a isopropanol ($(CH_3)_2CHOH$)–monoethanolamine (MEA: $H_2NCH_2CH_2OH$) solution at room temperature. The molar ratio of MEA to zinc acetate was kept to 1.0 and concentration of zinc acetate was 0.3 to 1.3 mol/l. The resultant solution was stirred at 50 °C for 1 h to yield a clear and homogeneous solution, which served as a coating solution. The coating was usually performed within 24 h after the solution was prepared. The films were prepared by spin-coating on glass (Corning Inc. 7059) substrate, which was rotated at 3000 rpm for 20 s. The films were preheated (baked) at several temperatures (200, 225, 250, 275 and 300 °C) for 10 min in a furnace to evaporate the solvent and remove organic residuals. The spin-coating to preheating procedure was repeated five times. The films were then post-heated (annealed) in furnace in air at 650 °C for 1 h. The thermal decomposition behavior of a ZnO sol solution was examined by thermogravimetry–differential thermal analyzer (TG–DTA: Seiko Exter 6000). The phases of ZnO thin film were determined by X-ray diffraction, using Rigaku Rotaflex D/max system with Cu Kα radiation ($\lambda = 0.154$ nm). The surface and cross section of the films were investigated by a scanning electron microscope (XL30 ESEM-FEG, FEI Company), using an electron beam energy of 15 kV. Optical transmittance was observed using UV–visible spectrometry (Hitach U3000), and the optical band gap energy was calculated from the data of the optical transmittance and wavelength. XPS measurements were carried out using a hemispherical energy analyzer and unmonochromated Mg Kα X-ray source ($h\nu = 1253.6$ eV). The base pressure in the XPS analysis chamber was under 10^{-10} Torr. The ZnO samples were sputter-cleaned by Ar ion bombardment about 5×10^{-7} Torr with an ion gun energy of 5 kV and a sample current of 10 μA to remove surface contaminants. The position of the C 1s peak was taken as reference with a binding energy of 284.5 eV. For the comparision, the O and Zn ratio was measured for a single crystal of ZnO which had been sputter-cleaned in the same method as the films, and this was taken to be the ideal O : Zn atomic ratio for ZnO films. The concentration ratio of O and Zn ($R_{O:Zn}$) was calculated as following equation $R_{O:Zn} = \{(I_{O1s}/I_{Zn3s})_{films}\} / \{(I_{O1s}/I_{Zn3s})_{ZnO\ crystal}\}$, where I_{O1s} and I_{Zn3s} are the integrated photoelectron peak areas in counts eV/s. The photoluminescence characteristics of ZnO thin films were evaluated by photoluminescence spectrofluorometry (SFM25, Kontron). A Xe lamp with a filter was used as the excitation light source with a wavelength of 270 nm and a power of 100 mW.

3. Results and discussion

Fig. 1 shows TG–DTA curves of the ZnO sol solutions. Weight losses were observed in three temper-

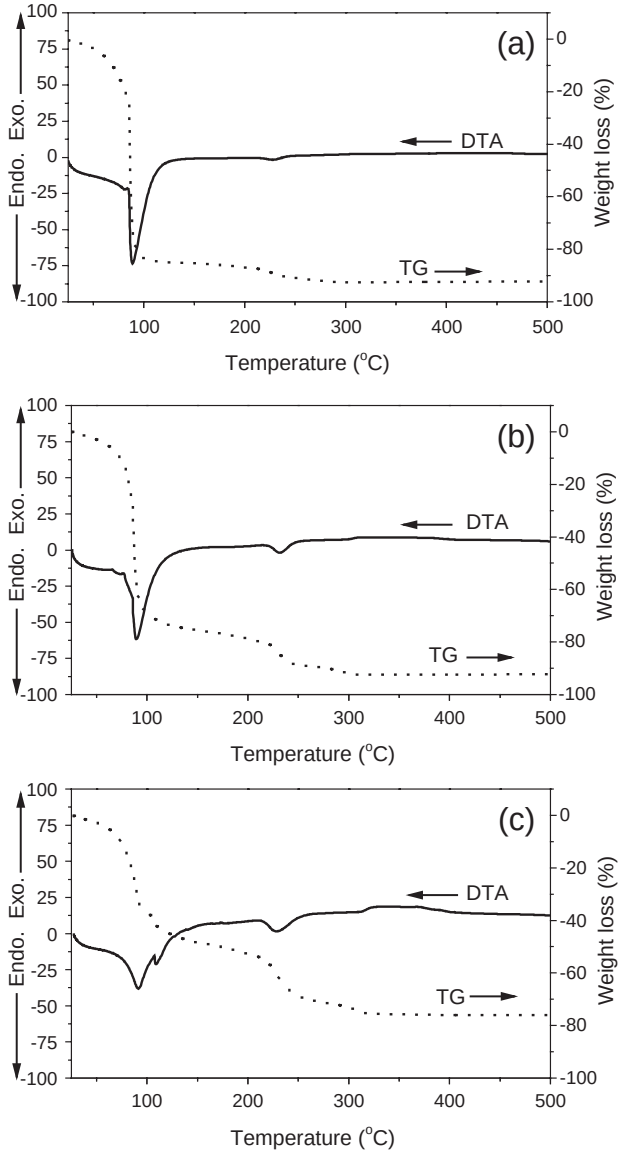

Fig. 1. TG/DTA curves of the ZnO sol solution with Zn concentration: (a) 0.3 mol/l, (b) 0.7 mol/l and (c) 1.3 mol/l.