Available online at www.sciencedirect.com
ScienceDirect
Ceramics International 34 (2008) 1237–1239
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

# Photoluminescence of ZnO layer on commercial glass substrate prepared by sol–gel process

Seung Hwangbo [a], Yun-Ji Lee [a,b], Kyu-Seog Hwang [b,*]

[a] Division of Electronic & Photonic Engineering, Honam University, 59-1 Seobong-dong, Gwangsan-gu, Gwangju 506-714, Republic of Korea
[b] Department of Biomedical Engineering and Institute of Photoelectronic Technology, Nambu University, 864-1 Wolgye-dong, Gwangsan-gu, Gwangju 506-824, Republic of Korea

Received 23 January 2007; received in revised form 5 February 2007; accepted 1 March 2007
Available online 18 April 2007

**Abstract**

Amorphous ZnO thin film on soda–lime–silica glass substrate was prepared by the sol–gel process at low-temperature processing, i.e., 100 °C. No distinct grain structure was observable in the surface of the film. The photoluminescence spectrum of the ZnO thin film with an intense near band edge emission was observed while the defect-related broad green emission was nearly quenched.


*Keywords:* ZnO thin film; Glass substrate; Sol–gel

## 1. Introduction

The most unique property of ZnO is its large exciton binding energy of 60 meV, which is much larger than those of GaN (24 meV), ZnSe (19 meV) and ZnS (39 meV) [1]. Owing to these properties, ZnO is considered as a promising material for light-emitting devices and semiconductor lasers with low thresholds in the ultraviolet (UV) region.

Using molecular beam epitaxy (MBE), rf magnetron sputtering, metal organic chemical vapor deposition (MOCVD) and other methods, high quality ZnO layers have been grown and their structural and optical properties have been extensively studied [2–5]. However, most of the reports on the UV emission of ZnO films have been concentrated on high-vacuum processes which are very expensive method from the viewpoint of system and source materials. To meet the industrial needs for the commercially available ZnO devices, the easier and cheaper deposition methods for the ZnO film should be developed. Sol–gel process is another attractive technique for obtaining thin films and has the advantages of easy control of the film composition and easy fabrication of a large-area thin film at low cost [6–9]. Until now, however, very few reports on the fabrication of ZnO film with a single violet emission by sol–gel have been published [10].

In this work, we first report a simple and efficient method to prepare amorphous ZnO thin films with intense UV emission on soda–lime–silica glass (SLSG) substrate.

## 2. Experimental

A homogeneous coating solution was prepared by mixing Zn acetate [$(CH_3COO)_2Zn{\cdot}2H_2O$] and 2-methoxyethanol ($HOCH_2CH_2OCH_3$). Since Zn acetate has a low solubility in 2-methoxyethanol, 2-aminoethanol ($H_2HCH_2CH_2OH$) (MEA) was added to obtain clear solution (concentration: 0.6 mol Zn acetate/L 2-methoxyethanol). The molar ratio of MEA to Zn acetate was fixed at 1.0. The mixing solution was stirred for 2 h to obtain a homogeneous sol.

The starting solution was spin-coated onto the cleaned substrate (25 mm × 25 mm × 1.7 mm) at 4000 rpm for 10 s in air. The as-deposited film was prefired at 100 °C for 10 min in air. The coating process was repeated 13 times to prepare a thick coating. Then the final annealing was performed in air at 100 °C for 60 min.

The crystallinity of the film was investigated by using a high resolution X-ray diffraction (HRXRD, X'pert-PRO, Philips, Netherlands). The thickness of the ZnO film was approximately 0.5–0.7 μm, as determined by observations of fracture

* Corresponding author. Tel.: +82 62 970 0110; fax: +82 62 970 0288.
*E-mail address:* khwang@nambu.ac.kr (K.-S. Hwang).

0272-8842/$34.00 
doi:10.1016/j.ceramint.2007.03.014

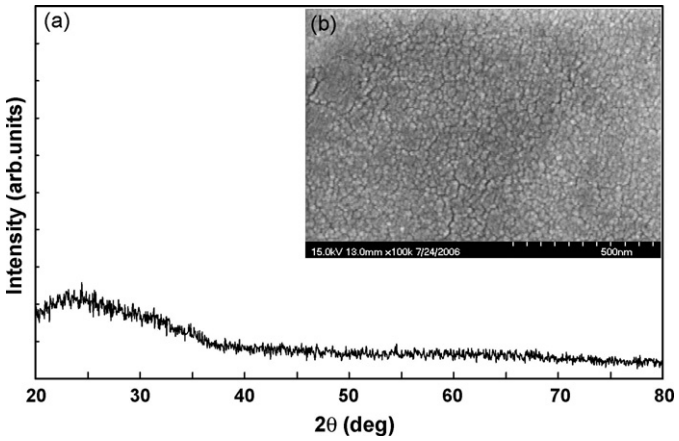


Fig. 1. (a) HRXRD spectra and (b) FE-SEM image of the ZnO thin film on SLSG substrate.

cross-sections with field emission-scanning electron microscope (FE-SEM). The surface morphology of the film was evaluated from a FE-SEM and a scanning probe microscope (SPM, PSIA, Republic of Korea). Room-temperature photoluminescence (PL) spectra of the sample were measured by micro-PL system (LabRamHR, Jobin Yvon, France) using 325 nm line of a He–Cd laser as the excitation source.

## 3. Results and discussion

Fig. 1(a) shows the XRD curve of ZnO thin film deposited on SLSG substrate. The film shows an amorphous pattern. Fig. 1(b) shows the FE-SEM photograph of the ZnO film after heat treatment at 100 °C. Particulate structure is indistinct. Crack-like texture and pores were unable to see on the surface of the film. There is no evidence of aggregation of particles.

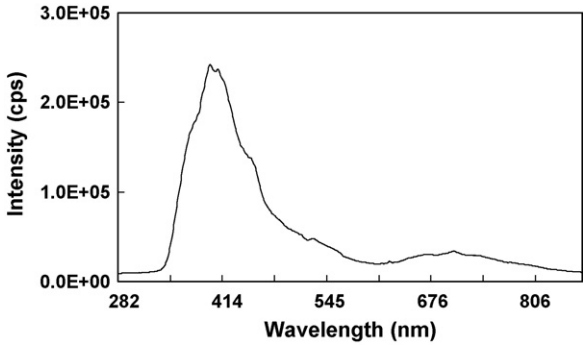


Fig. 3. Room-temperature PL spectrum for the ZnO thin film on SLSG substrate heat treated at 100 °C.

Fig. 2 shows typical SPM micrograph (1 μm × 1 μm) of the ZnO thin film obtained at 100 °C. To obtain more exact roughness data, we performed five analyses at different area per each sample. We can observe relatively regular and uniform surface structure of the film.

The PL spectra at room temperature of amorphous ZnO thin film on SLSG substrate obtained by pyrolysis and annealing at 100 °C is shown in Fig. 3. In the PL spectra, an intense near-band-edge (NBE) emission is seen. This NBE peak has been previously attributed to the emission from free exciton in the literature [11]. A faint defect-related broad green (deep-level) emission is seen. The origin of the green luminescence is still in dispute, but it is usually attributed to emission related to grain boundary defects and other interior defects such as oxygen vacancy ($V_O$) and impurities [12].

Apparently, for the film annealed at low temperature, 100 °C, the FWHM value of the PL spectrum curve was about 50 meV and this value is believed to be comparable with any previously reported values of ZnO films prepared by the sol–gel process.

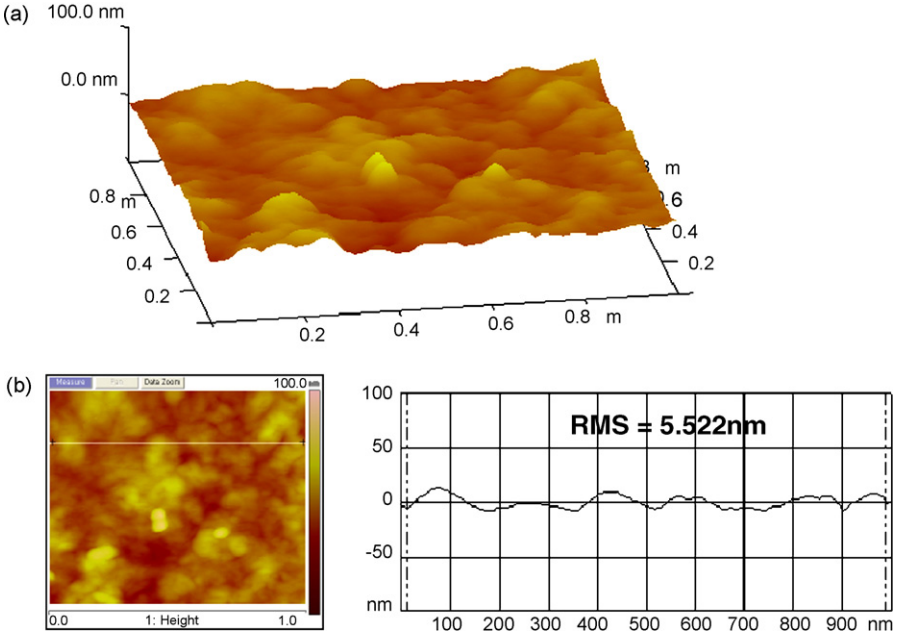


Fig. 2. SPM image for the film after annealing at 100 °C.

The PL spectrum of amorphous ZnO thin films with intense UV emission was observed while the visible emission was nearly quenched. The features can be explained reasonably by Wang et al. as follows [10]: (i) the higher degree of disorder likely leads to intensity emission stronger than that of crystalline ZnO. (ii) Quantum confinement effects (QCE) occur when the particle radius is of the order the exciton Bohr radius (1.8 nm, ZnO).

It is well understood that PL spectra depend on the stoichiometry and the microstructure of the film. Therefore, these results indicate that the obtained amorphous ZnO films at low temperature are well close to stoichiometry and of optically high quality. Our findings show that the ZnO films prepared by sol–gel route at 100 °C can be one of the promising candidates for the UV optical devices on flexible plastic substrates.

## 4. Conclusions

In this study, amorphous ZnO thin film was grown on inexpensive SLSG substrates using a sol–gel process. From XRD analysis, the film exhibited an amorphous structure. From the PL measurement, an intense NBE emission was observed, while the deep-level emission is obviously faint. These results indicate it should be possible to cheaply and easily fabricate ZnO-based optoelectronic devices at low temperature, below 100 °C, in the future.

## References

[1] Y.F. Chen, D.M. Bagnall, H.J. Koh, K.T. Park, K. Hiraga, Z. Zhu, T. Yao, J. Appl. Phys. 84 (7) (1998) 3912–3918.
[2] H. Tampo, A. Yamada, P. Fons, H. Shibata, K. Matsubara, K. Iwata, S. Niki, K. Nakahara, H. Takasu, Appl. Phys. Lett. 84 (22) (2004) 4412–4414.
[3] K.K. Kim, J.H. Song, H.J. Jung, S.J. Park, J.H. Song, J.Y. Lee, J. Vac. Sci. Technol. A 18 (6) (2000) 2864–2868.
[4] W.I. Park, S.J. An, G.C. Yi, H.M. Jang, J. Mater. Res. 16 (5) (2001) 1358–1362.
[5] L. Wang, Y. Pu, W. Fang, J. Dai, C. Zheng, C. Mo, C. Xiong, F. Jiang, Thin Solid Films 491 (2005) 323–327.
[6] Y. Natsume, H. Sakata, Thin Solid Films 372 (2000) 30–36.
[7] R. Ayouchi, D. Leinen, F. Martin, M. Gabas, E. Dalchiele, J.R. Ramos-Barrado, Thin Solid Films 426 (2003) 68–77.
[8] P. Nunes, E. Fortunato, R. Martins, Thin Solid Films 383 (2001) 277–280.
[9] F. Paraguay D., J. Morales, W. Estrada L., E. Andrade, M. Miki-Yoshida, Thin Solid Films 366 (2000) 16–27.
[10] Z. Wang, H. Zhang, Z. Wang, L. Zhang, J. Yuan, S. Yan, C. Wang, J. Mater. Res. 18 (1) (2003) 151–155.
[11] W.I. Park, G.C. Yi, J. Electron. Mater. 30 (2001) 32.
[12] D.C. Look, D.C. Reynolds, J.R. Sizelove, R.L. Jones, C.W. Litton, G. Cantwell, W.C. Harsch, Sold State Commun. 105 (1998) 399.