

## Comparative study on structural and luminescence properties of solution processed ZnO thin films

***Byung-yoon Park<sup>\*,a,b</sup>, Sungho Choi<sup>a</sup>, Chang Seop Hong<sup>b</sup>, Beyong-Hwan Ryu<sup>a</sup>  
and Ha-Kyun Jung<sup>a</sup>***

<sup>a</sup>Advanced Materials Division, Korea Research Institute of Chemical Technology,  
P.O. Box 107, Yuseong, Daejeon 305-600, Korea

<sup>b</sup>Dept. of Chemistry, Korea University,  
Anam-dong, Seongbuk-gu, Seoul 136-701, Korea  
Phone: +82-42-860-7313, E-mail: [genius@kriict.re.kr](mailto:genius@kriict.re.kr)

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### Abstract

*Film morphology, crystallinity, and luminescence property of solution processed ZnO films have been studied. Fluorine addition and annealing ambient significantly change the defect-related emission band as well as the structural property. Using the overall emission behaviors, we can predict an optimized process condition for solution-based ZnO thin film.*

### 1. Introduction

Zinc oxide (ZnO) is a promising material for display, solar cells, gas sensors and other optoelectronic devices. It has several advantages such as low resistivity, high transmittance, and abundance in natural resource. Several approaches have been proposed for the preparation of ZnO thin films such as thermal deposition, sputtering, chemical vapor deposition, dip-coating and spray pyrolysis [1,2].

Recently, the solution-based film growth is an attractive method because of the following reasons: good homogeneity, ease of composition control, and large area coatings with cost effective process equipment. Therefore, solution-based process enable us to produce low cost thin film transistor manufacturing for vast electronic applications of immense commercial implications as they can be deposited/patterned using conventional low cost solution techniques [3].

In general, thin film ZnO tends to exhibit many

defects, such as oxygen vacancy, zinc interstitial, zinc vacancy, interstitial oxygen and antisite oxygen, which might control the overall structural, optical and electrical properties of ZnO thin films [4-6]. Especially, the oxygen vacancy is known as a dominant defect sites inducing n-type semiconductor property [7].

In this study, we investigated the structural and luminescence properties of spin-coated ZnO thin films prepared with various synthetic conditions. Effects of fluorine incorporation on the luminescence properties are presented. It was observed that film crystallinity and defect related emission characteristics were strongly dependent on solvent composition, additives and annealing ambient.

### 2. Experimental

ZnO thin films were grown on the quartz substrates by solution-based process. The precursor solution was basically prepared using Zinc acetate dehydrate ( $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ ), 2-methoxyethanol ( $\text{C}_3\text{H}_8\text{O}_2$ , 2-ME), and monoethanolamine ( $\text{C}_2\text{H}_7\text{NO}$ , MEA). 2-ME, IPA and MEA were used as the solvent and stabilizing agent, respectively. Ammonium fluoride ( $\text{NH}_4\text{F}$ ), zirconium fluoride ( $\text{ZrF}_4$ ), and lithium fluoride ( $\text{LiF}$ ) were properly used as fluxing agents. The 0.2M Zinc acetate dihydrate was first dissolved in a mixture of 2-ME and MEA solution stirring at room temperature. The molar ratio of MEA:Zn ( $\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  is 1:1. The solution was thoroughly mixed at room temperature to get a clear and homogeneous precursor.

And then various fluoride compounds, such as  $\text{NH}_4\text{F}$ ,  $\text{ZrF}_4$  and  $\text{LiF}$  were added.

The precursor was dropped on the quartz substrates which were spun at 2650 rpm for 30s. The films were preheated in air at 180 °C. The process was repeated 10 times to get 100 nm thick ZnO films. As grown ZnO films have been annealed at various annealing ambient, air,  $\text{O}_2$ ,  $\text{N}_2$ , and 5%  $\text{H}_2$  flow rate of 500 sccm at 400 °C for 1h.

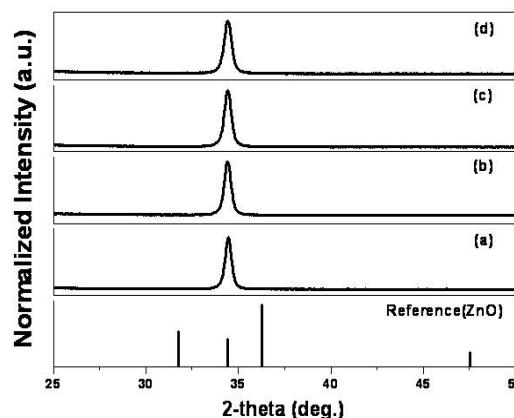
Crystallinity of all prepared ZnO thin films were characterized by using XRD-Rikaku DMAX-33 X-ray diffractometer with Cu K $\alpha$  ( $\lambda=1.5406$  Å) radiation. The surface and cross-section morphology of the thin film was scanning electron microscopy. The photoluminescence (PL) spectra of the product were measured using a luminescence spectrometer at room temperature with a He-Cd laser (325 nm) as excitation source.

### 3. Results and discussion

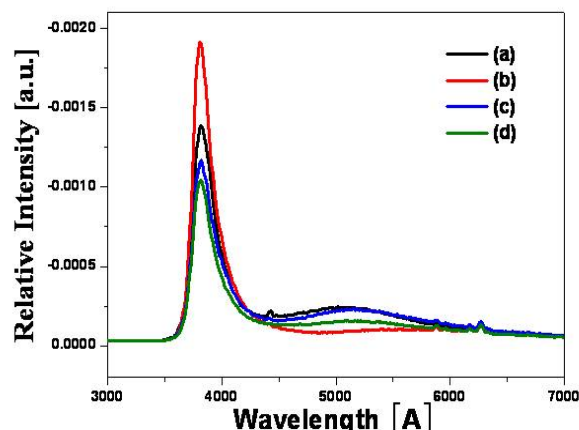
Fig. 1 summarizes the X-ray diffraction peaks of ZnO thin films prepared under various annealing ambient. All samples show only a prominent (002) peak positioned at  $2\theta=34.4^\circ$ , which means that spin-coated ZnO films in our synthetic conditions were grown along the c-axis orientation irrespective of different annealing ambient. This is meaningful that all the corresponding ZnO films are formed in effective state which gives proper channel mobility.

Fig. 2 shows the emission spectra of corresponding ZnO thin films. It can be seen that all samples show a typical luminescence behavior with the two emissions of a narrow UV peak positioned at 382 nm and a broad band centered around 480~600 nm [8]. The relative emission intensity of a sharp UV emission peak which corresponds to the exciton emission from near conduction band to valence band substantially changed with varying anneal ambient. The tendency becomes more obvious anneal with increased oxygen partial pressure, which should be an indication of film stoichiometry is improved. Additionally, a broad band within visible wavelength region corresponding to the various internal defect sites, such as zinc interstitial and oxygen vacancy substantially decreased anneal under higher oxygen partial pressure (specially in sample (b)). Therefore, it demonstrates that dominant defect sites related to a broad emission band is oxygen

vacancy in solution-processed ZnO films [9].

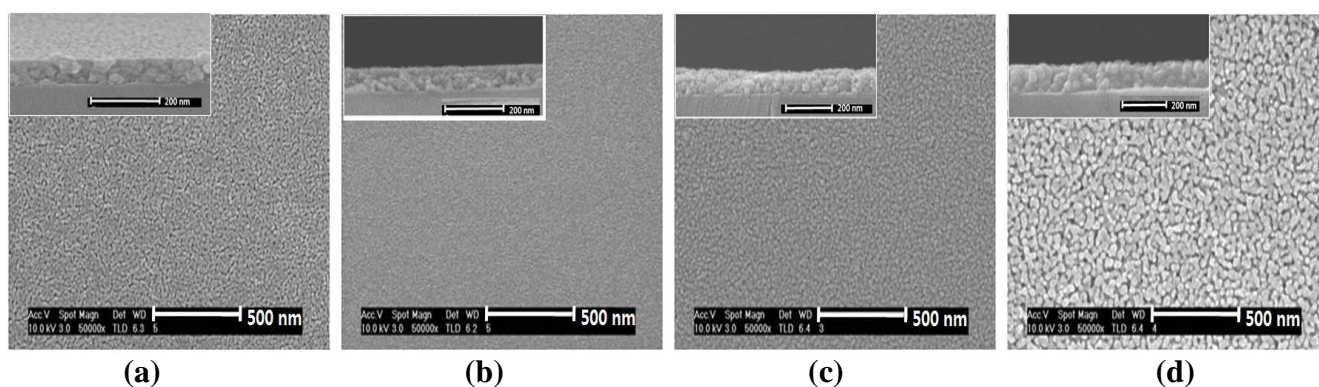


**Figure. 1** XRD patterns of ZnO thin films annealed at various ambient; (a) air, (b)  $\text{O}_2$ , (c)  $\text{N}_2$ , and (d) 5%  $\text{H}_2$



**Figure. 2** PL spectra of ZnO thin films annealed at various ambient; (a) air, (b)  $\text{O}_2$ , (c)  $\text{N}_2$ , and (d) 5%  $\text{H}_2$

Fig. 3 shows the images of the corresponding ZnO films prepared by using different fluoride additives. Film thickness of all prepared ZnO layer is roughly 100 nm, as shown in each cross-sectional image. It clearly shows that using different fluoride addition



**Figure. 3** Cross sectional and plane view SEM images of ZnO film with various fluoride compound addition. (a) add  $\text{NH}_4\text{F}$  (air anneal) (b) add  $\text{LiF}$  (air anneal) (c) add  $\text{ZrF}_4$  (air anneal) (d) add  $\text{ZrF}_4$  with UV pre-cured substrate (air anneal)

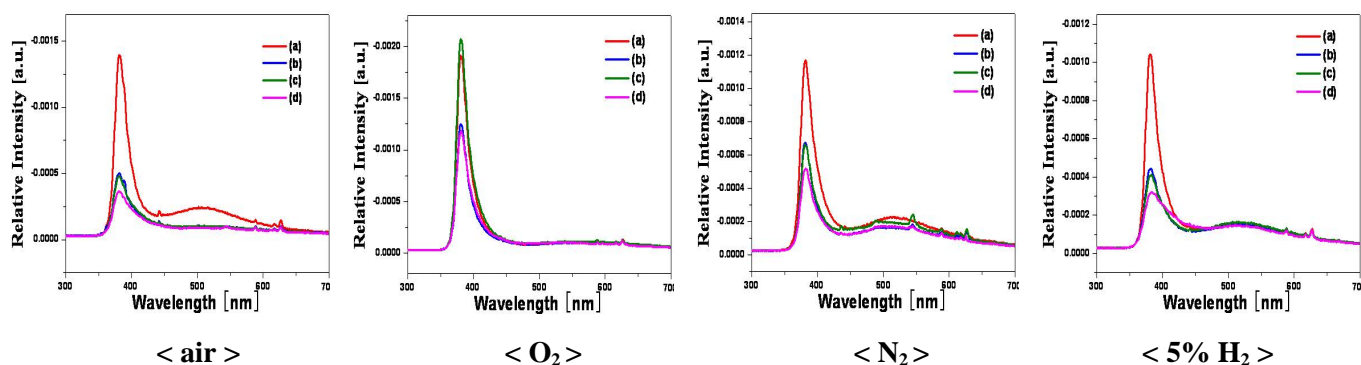
leads to modified surface morphology and film crystallinity. This result implies that an effective fluxing effect occurs during post-annealing processes. Surface condition can also affect the overall film morphology as well. As seen in Fig. 3(d) the grain size is substantially increased coated on UV pre-cured quartz substrate. The larger grain size means less number of grain boundary and defect density, which improve the electrical and luminescence properties of solution-based thin films [10].

Fig. 4 shows the room temperature photoluminescence spectra of ZnO films with addition of various fluorides annealed under different ambient. In case of air anneal, fluorine-doped samples illuminated only UV emission with substantially decreased emission intensity. On the contrary, films annealed under oxygen ambient exhibit enhanced UV emission without defect-related emission. Therefore, we can control both the stoichiometry and the defect-related

emission property of spin-coated ZnO film with varying anneal ambient and proper fluorine addition. Taking into consideration the decreased defect-related emission shown in air anneal Fig. 4, it can be concluded that fluorine incorporation in the ZnO films is properly taking place at oxygen sites same as that of oxygen dominant anneal ambient.

In case of anneal under nitrogen and hydrogen ambient, however, no significant change of defect-related emission.

Table. 1 summarizes the PL intensity ratio of the defect-related emission (480~600 nm) to exciton emission (380 nm) of ZnO thin films prepared with different solution conditions. For ZnO films annealed in oxygen ambient, the ratio of  $I_{500}/I_{380}$  was much smaller than other cases. This means that the degree of oxygen partial pressure in annealing ambient plays a key factor to control the overall emission behavior of solution-processed ZnO films.



**Figure. 4** PL spectra of spin-coated ZnO thin film prepared under various anneal ambient. (a) without fluoride, (b) add  $\text{NH}_4\text{F}$ , (c) add  $\text{ZrF}_4$ , (d) add  $\text{LiF}$

anneal ambient sample	$I_{\text{visible}}/I_{\text{uv}}$			
	air	O <sub>2</sub>	N <sub>2</sub>	5% H <sub>2</sub>
(a)	0.173	0.050	0.188	0.133
(b)	0.193	0.076	0.263	0.314
(c)	0.193	0.046	0.300	0.340
(d)	0.253	0.081	0.337	0.434

**Table. 1** PL emission intensity ratio of the visible (480~600 nm) to UV (380 nm) with various annealing ambient. (a) without fluoride, (b) add NH<sub>4</sub>F, (c) add ZrF<sub>4</sub>, (d) add LiF

#### 4. Summary

Understanding the structural property and luminescence phenomena related to prevailing defects in solution-processed ZnO film are essential to obtain the optimum process condition and the electrical properties can be tuned by this approach.

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