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## Structural and Photoluminescence Properties of ZnO Thin Films Deposited by Ultrasonic Spray Pyrolysis

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### Abstract

Zinc oxide (ZnO) thin films on a silicon (Si) (111) substrate were grown herein using ultrasonic spray pyrolysis at 450 °C with different Zn concentrations. The ZnO thin films had X-ray diffraction patterns of a polycrystalline hexagonal wurtzite structure. The (002) and (101) peak intensities changed under different Zn concentrations. Furthermore, according to Scherer's and Stokes–Wilson equations, the crystallite size and the internal strain of the ZnO thin films in the (002) and (101) peaks changed with the Zn concentration. Optically, the photoluminescence spectra indicated that the ratio of the UV/GB emission of the ZnO thin films was the highest at the Zn concentration of 0.02 mol/mL. We predicted that by increasing the Zn concentrations, the nonradiative transitions, which originated from defects, such as lattice and surface defect, become dominant. In conclusion, the ZnO thin films with the Zn concentration of 0.02 mol/mL had a better crystalline and optical quality.

### Abstrak

**Karakteristik Struktur dan Fotoluminisen dari Lapisan Tapis ZnO yang Dideposisikan menggunakan Pengkabutan Ultrasonik.** Lapisan tipis seng oksida (ZnO) telah ditumbuhkan di atas substrat silikon (111) menggunakan pengkabutan ultrasonik dengan variasi konsentrasi Zn pada suhu 450 °C. Berdasarkan pengujian difraksi sinar-X, lapisan tipis ZnO memiliki struktur wurtzite berbentuk hexagonal polikristalin. Dua buah puncak yang memiliki orientasi bidang (002) dan (101) memiliki perubahan intensitas akibat adanya variasi konsentrasi Zn. Begitupula hasil perhitungan yang mengacu pada persamaan Scherer's dan Stokes-Wilson, memberikan informasi bahwa ukuran kristallite dipengaruhi oleh konsentrasi Zn. Secara optik, perbandingan emisi UV/GB yang teramati dari spektrum fotoluminisen memiliki nilai tertinggi ketika konsentrasi Zn 0.02 mol/mL. Kami memprediksikan bahwa penambahan konsentrasi Zn, transisi *non-radiative* yang berasal dari defek-defek (defek kisi dan permukaan) menjadi dominan. Sebagai kesimpulan, lapisan tipis ZnO yang memiliki konsentrasi Zn 0.02 mol/mL memiliki kualitas kristal dan optik yang lebih optimal.

*Keywords: photoluminescence, thin films, USP, XRD, ZnO*

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### 1. Introduction

Zinc oxide (ZnO) is a semiconductor material with a wide band gap energy (3.4 eV) and a strong exciton binding energy (60 meV). Even though the ZnO band gap energy is almost the same with GaN, the exciton binding energy is much higher compared to that of ZnS (20 meV) and GaN (25 meV) [1]. Therefore, ZnO has a broad range of applications, such as solar cells [2], light-emitting devices (LED) [3], and photodetectors [4]. Furthermore, ZnO is a promising semiconductor material

for short-wavelength ZnO, especially for ultraviolet (UV) light-emitting diodes (LEDs) and laser diodes (LDs) [5].

In the past decade, ZnO thin films were fabricated using various methods (i.e., metal organic vapor deposition, molecular beam epitaxy, pulsed laser decomposition, sputtering, phase vapor transport, and ultrasonic spray pyrolysis (USP)) [6]. Among these methods, the USP offers simplicity and low cost for fabricating thin films [7, 8].

Furthermore, the structure and the optical and electrical properties of ZnO thin films are strongly influenced by the growth temperature, precursor molarity, and deposition time [9]. Various substrates were used to investigate the properties of the ZnO film crystallinity and lattice mismatch [10]. The Si substrate is always attracting great attention in realizing the integration of an emitting device on the Si technology. Moreover, Si has the prominent merits to make the driving voltage of the LED lower and the cost of the devices to be less expensive [11].

Photoluminescence (PL) is very important and useful in studying the optical properties of ZnO thin films. Therefore, the PL properties of ZnO are still a major interesting subject because of the existence of natural defects that are responsible for visible band emissions. Furthermore, the PL properties of ZnO thin films depend on the preparation methods, growth conditions, chemical composition, and post-growth treatment [11, 12].

In this study, we deposited ZnO thin films on top of a Si (111) substrate using USP with different Zn concentrations.

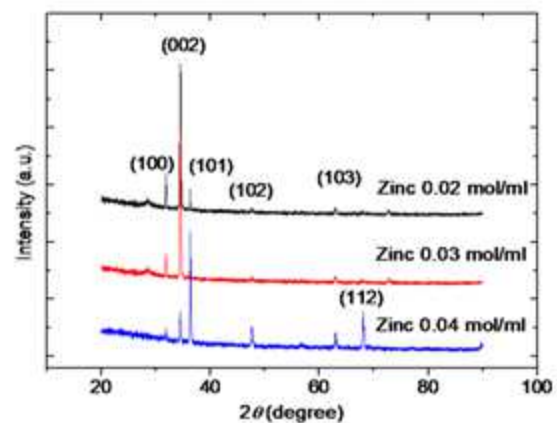
## 2. Experimental

Undoped ZnO thin films were deposited on a p-type Si (111) substrate using USP with different Zn concentrations. Zinc acetate dehydrate ( $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ ) was chosen as the precursor. Zn concentrations of 0.02, 0.03, and 0.04 mol/mL were diluted in deionized water. The aerosol of the precursor's solution was generated by commercial USP with a constant frequency of 1.7 MHz. It was then transported to the heated Si substrate at a temperature of 450 °C for 15 min. The crystal structure and the photoluminescence properties of the ZnO thin films were characterized by X-ray diffraction (XRD) using Shimadzu 7000 with Cu  $\alpha$  radiation and an FLS920 photoluminescence spectrometer (Edinburgh Instruments), respectively.

## 3. Results and Discussion

Figure 1 shows the XRD spectra of the ZnO thin films with different molarities at a growth temperature of 450 °C for 15 min. According to the International Center for Diffraction Data (ICDD) number 36-1451 and the inorganic crystal structure database (ICSD #: 067849), the ZnO thin films had a polycrystalline hexagonal wurtzite structure.

Five peaks were observed with the (002), (101), (102), (103), and (004) orientations for the Zn concentration of 0.02 mol/mL, while seven peaks were found with the (100), (002), (101), (102), (100), (103), and (112) orientations for the Zn concentrations of 0.03 and 0.04 mol/mL. Hence, the number of orientation increased when



**Figure 1. XRD Spectra of The ZnO Thin Films with Different Zn Concentrations**

the Zn concentration increased. Nevertheless, the quality of the polycrystalline ZnO thin films can be affected by the number of Zn molarities. Figure 1 shows that the crystalline quality for the ZnO thin film with a Zn concentration of 0.02 mol/mL was better than that with 0.03 mol/mL and 0.04 mol/mL. The peak orientation of the polycrystalline ZnO thin films was most intense at (002) when the Zn concentration was 0.02 mol/mL. In contrast, the crystal peak orientation (101) of the polycrystalline ZnO thin films was dominant when the Zn concentrations were 0.03 and 0.04 mol/mL.

The full width at half maximum (FWHM) of the ZnO thin films can be used to predict the crystallite size ( $D$ ) using Scherer's equation [13].

$$D = \frac{0.94 \lambda}{\beta \cos \theta} \quad (1)$$

According to Scherer's equation,  $\lambda$  is the wavelength of the XRD;  $\beta$  is the FWHM of the diffraction peak; and  $\theta$  is the diffraction angle. The (002) and (101) peaks were used to compare the crystallite size evolution caused by the Zn concentration. According to the XRD spectrum, the Zn concentration induced the number of unit cells in the (002) and (101) planes to be different. The (002) peak intensity decreased with the increasing Zn concentration. Meanwhile, the (101) peak intensity increased with the increasing Zn concentration.

Accordingly,  $\beta$  of the XRD peaks contained contributions from the crystal size and the lattice strain.  $\beta$  of the ZnO thin films with Zn concentrations of 0.02, 0.03, and 0.04 mol/ml in the (002) and (101) planes were 0.2, 0.16, and 0.14 nm and 0.25, 0.19, and 0.17 nm, respectively.

The average strain of the ZnO thin films was calculated using the Stokes–Wilson equation [14].

$$\varepsilon = \frac{\beta}{4 \tan \theta} \quad (2)$$

The crystallite size and the internal strain of the ZnO thin films were calculated using the Williamson–Hall assumption. Figure 2 shows the crystallite size and the internal strain of the ZnO thin films in the (002) and (101) planes as a function of the Zn concentration. Figure 2 shows that the crystallite size and the internal strain of the ZnO thin films in the (002) were 33.2, 54.2, and 41.3 nm and 0.20, 0.22, and 0.24, respectively. Meanwhile, the crystallite size and the internal strain of the ZnO thin films in (101) were 32.8, 40.8, and 46.3 nm and 0.31, 0.26, and 0.25, respectively. The crystallite size and the internal strain non-linearly varied with the increasing Zn concentrations. Meanwhile, the crystallite size of the ZnO thin films in (101) increased when the Zn concentration increased. It can be predicted that defects, such as Zn interstitial, O vacancy, and Zn antisite, were not equally distributed in the ZnO structure.

Figure 3 depicts the room temperature PL spectra of the ZnO thin films with different Zn concentrations. The PL spectra showed typical ZnO properties, which consisted of two major peaks at 378 nm and 510 nm. A strong PL emission peak was observed at 378 nm corresponding to the UV emission. The UV emission of the ZnO thin films should be caused by an exciton-related activity [15,16]. Meanwhile, the green (GB) emissions were mainly caused by defects, such as oxygen vacancies [12]. The ratio of the PL intensities of the UV to GB emissions was presented

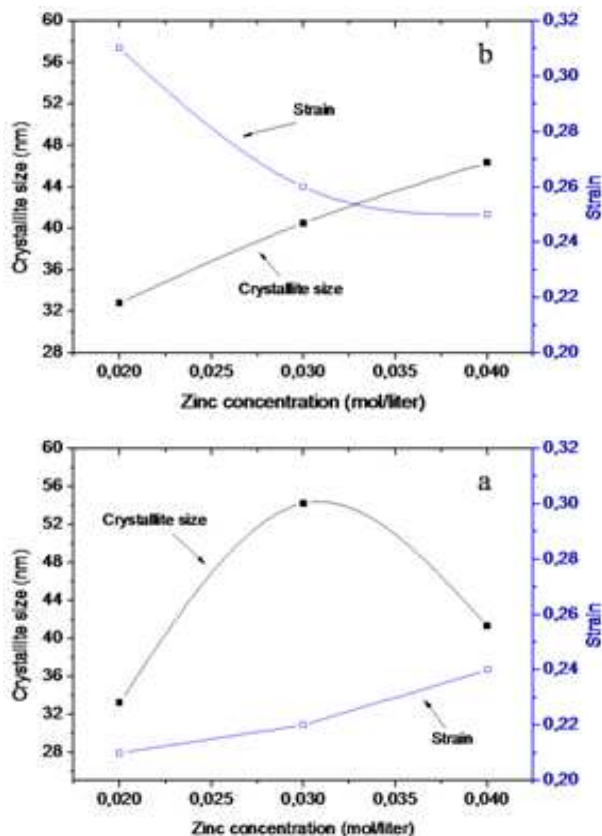


Figure 2. Crystal Size and Strain in the a) (002) and b) (101) Planes as a Function of the Zn Concentration

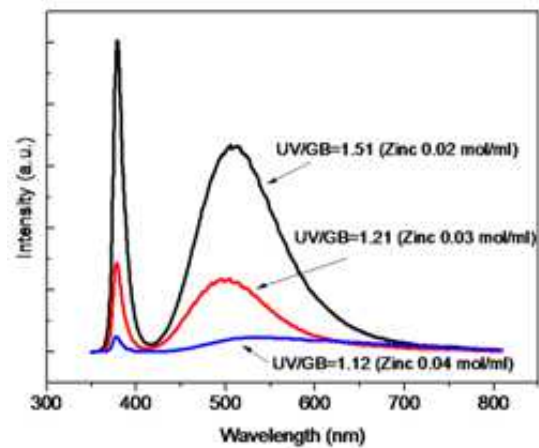


Figure 3. Room Temperature PL Spectra of the ZnO Thin Films with Different Zn Concentrations

in the figure to investigate the defect contribution to these emissions [17]. The UV/GB emission ratios of the ZnO thin films with Zn concentrations of 0.02, 0.03, and 0.04 mol/mL were 1.51, 1.21, and 1.12, respectively. Both the UV and GB intensities increased with the decreasing zinc concentrations. The emission intensity was generally determined by the radiative and nonradiative transitions [16]. The nonradiative transition was induced by point defects, dislocations, and grain boundaries [16]. According to the UV/GB ratio, the ZnO thin films with the lowest Zn concentration (i.e., 0.02 mol/ml) had the highest ratio.

The excess of Zn was predicted to induce the lattice and surface defect, which produced the nonradiative transitions. As a result, the emission intensity of the GB was suppressed by its transitions. Under the same condition, the binding energy of exciton became weaker because of the nonradiative transitions.

#### 4. Conclusions

We deposited herein ZnO thin films with different Zn concentrations using USP. The XRD spectra confirmed that the ZnO thin films had a polycrystalline hexagonal wurtzite structure. The (002) and (101) peak intensities changed under different Zn molarities. Meanwhile, the crystallite size increased, and the internal strain of the ZnO thin films in the (002) and (101) peaks changed with the Zn concentration. Therefore, according to the XRD spectra, the ZnO thin film with the Zn concentration of 0.02 mol/ml has a better crystalline quality. Optically, the PL spectra indicated that the ratio of the UV/GB emission of the ZnO thin films was the highest at the Zn concentration of 0.02 mol/mL. By increasing the Zn concentration, the nonradiative transitions, which originated from defects (e.g., lattice and surface defect), were predicted to become dominant. As a result, the UV and GB emissions were suppressed by the increasing Zn concentration.

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