

# Optical and Defect Properties in Nearly Stoichiometry ZnO Film Coated on Si (111) by Ultrasonic Spray Pyrolysis Method

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**ABSTRACT**— ZnO is one of ceramic semiconductor material, which has interesting properties due its wide bandgap energy (3.4 eV), and it may be used in many optoelectronic devices. Optical and Defects properties of ZnO could affect the properties of the devices. ZnO films have been deposited on Si (111) substrate by ultrasonic spray pyrolysis (U.S.P.) method at temperatures 400°C, 450°C, and 500°C. The samples consist of two part, annealed and non-annealed heat treatment. The annealed treatment was conducted at temperature 800°C for 2 hours. The XRD pattern revealed that the ZnO film is a polycrystalline. The T.E.M. characterization showed that non stoichiometry of the ZnO film present. From the UV-vis pattern, the transition of electrons is affected by the defect present. The ZnO films show a characteristic luminescence properties. It found three defects, there are oxygen vacancies ( $V_o$ ), oxygen interstitial ( $O_i$ ), and an electron transition from the level of the ionized oxygen vacancies to the valence band, that is responsible for green band emission.

**Keywords**— ZnO film, Ultrasonic Spray Pyrolysis , Defect, optical

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## 1. INTRODUCTION

ZnO is ceramic semiconductor material. It has interesting properties because of its wide bandgap energy (3.4 eV) and it has also large exciton binding energy (60 meV) [1,2]. Their properties are also attractive because ZnO may be used in many devices such as devices in Photocatalytic, Optoelectronic, and Textile [3,4]. Previous research show that ZnO film have been carried out by many method such as molecular beam epitaxy (M.B.E.) [5], metal-organic chemical vapor deposition (MOCVD) [6], sputtering [7], pulsed laser deposition (PLD) [8], chemical vapor deposition (CVD) [9]. One these method is ultrasonic Spray Pyrolysis (U.S.P.) which is low cost and simple method to get a good ZnO films on many type of substrate [10]. ZnO ceramic materials show Photoluminescence phenomena in the U.V. and Visible region [11]. Previous results reported that these phenomena U.V. is originate from band to band transition and free exciton recombination [12], and the visible region may be predicted from the existence of native defect [13]. But, the mechanism the visible luminescence is unfinished.

Thermal annealing is a heating process at certain temperature for certain time. During annealing, the atom of the materials may move or diffuse in order to rearrange the position to have the lowest energy. Thermal annealing is usually

used in a semiconductor material to activate the dopant and to improve crystal quality. In other research thermal annealing of undoped ZnO and doped ZnO films were conducted in various temperature and time [14]. Various defect, such as Vacancy, Interstitial, dislocation, and other structural defects may move in the bulk material and absorption/decomposition may also occur on the surface. Hence, the structure and stoichiometric ratio of the material may also change [14]. Therefore, all of these changes will affect Optical properties.

In this paper, we study the optical properties and the existence of defects of ZnO films grown on Si(111) substrate by the U.S.P. method. The phenomena of the defect is interesting to be studied because it may control the donor or acceptor in ZnO thin films [15].

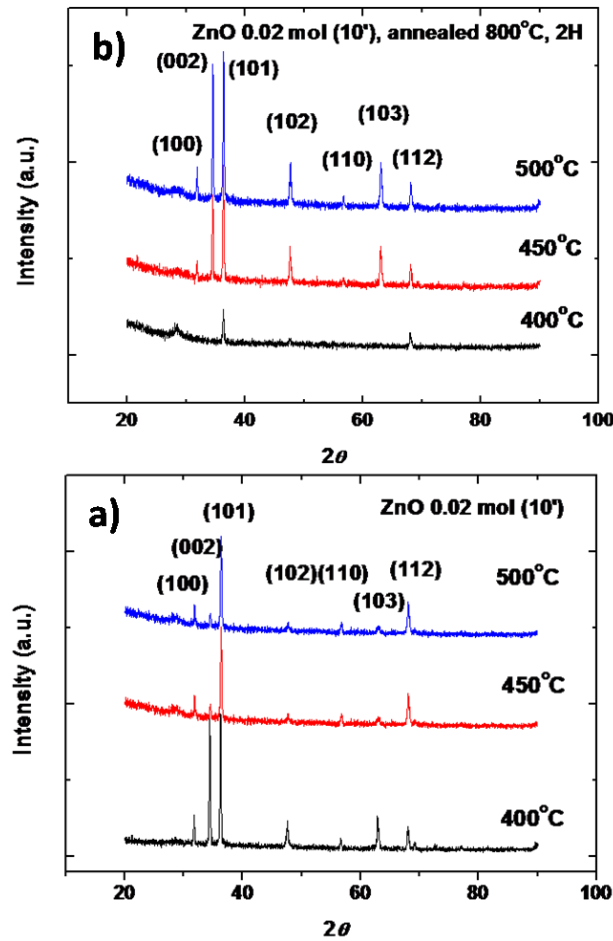
## 2. MATERIALS AND METHOD

Zinc acetate dehydrate [ $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ ] was used as a precursor materials. This materials was diluted in de-ionized water in concentration (0.02 mol/ml). Ultrasonic Spray Pyrolysis (USP) was used to deposit ZnO solution on *p*-type Si(111) substrates. The aerosol of the precursor for each solution were then injected onto a Si (111) substrate while heated at temperature, 400°C, 450°C, and 500°C for 10 minutes. Then, some of the samples were annealed at 800°C for 2 hours at atmosfer ambient. The structure, morphology, photoluminescence, optical absorbance of the non annealed and annealed ZnO films were characterized by using by X-ray diffraction (XRD 7000 Shimadzu), Transmission electron Microscope, Renishaw micro-PL system with 325 nm He-Cd laser as the excitation source, and spectrophotometer Vis-NIR ocean optics USB 1000 oceanoptic, respectively.

## 3. RESULTS AND DISCUSSION

### 4.1 X-ray Diffraction

X-ray diffraction were used to determine phase and the structure of the film. Figure 1 shows the XRD pattern of ZnO films grown by ultrasonic spray pyrolysis (USP) with growth temperatures 400°C, 450°C, and 500°C. It is seen that the non annealed and annealed ZnO films at 800°C for 2 hours shows the phase of ZnO. There are seven diffraction peaks which observed at  $2\theta = 31.7^\circ, 34.7^\circ, 36.3^\circ, 47.6^\circ, 56.5^\circ, 63^\circ, 68.1^\circ$ .



**Figure 1 :** XRD pattern of ZnO films 0.02 mol at growth temperatures 400°C, 450°C, and 500°C, a) non-annealed, b) annealed at 800°C for 2 hours

The peaks observed are related to (100), (002), (101), (102), (110), (103), (112) plane, respectively. The (002) and (101) plane of the ZnO film have the most higher peaks. Nevertheless, the peaks of ZnO thin films at growth temperature 400°C is reduced by annealing. It indicate that absorption/decomposition process during annealing may occur on the surface of ZnO films at growth temperature 400°C.

#### 4.2 Transmission Electron Microscope (TEM) X-ray Diffraction

Transmission Electron Microscope was used to observed the morphology, the phase and the ratio of Zn and Oxygen element. . Selected area electron diffraction (SAED) pattern which was taken from the corresponding area of ZnO deposit at temperature 450 °C and annealed at 800 °C for 2 hours is shown in Figure 2. JEMS software was used to identify the phase of the pattern. It reveals the presence of ZnO, which correspond to ICSD 164690 crystallography base data. Small ring radius deviation detected on the SAED may indicate that the stoichiometry does not fit 100% with ZnO. It indicate the present of atomic defect.

The particle size and shows E.D.X. line scan was taken from one particle of ZnO (Figure 3). The particle has a size of around 20 nm. The element concentration of Zn and Oxygen are not fit to 1 : 1 along the line. It indicates the existences of defect.

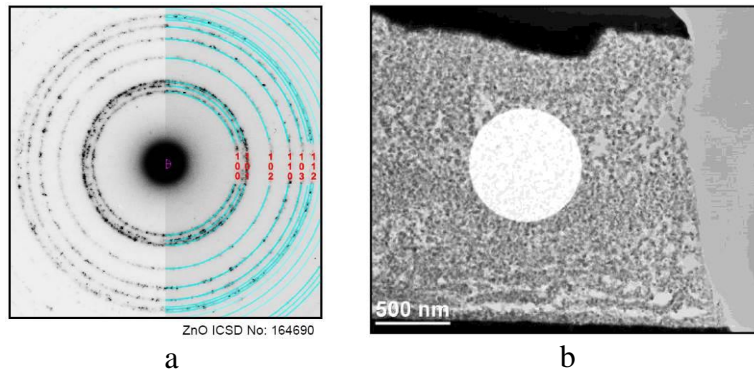


Fig. 2. Selected Area Electron Diffraction (SAED) (a) pattern taken from the corresponding area of  $Zn_xO_y$  (b) deposit at temperature 450°C and annealed at 800 °C for 2 hours.

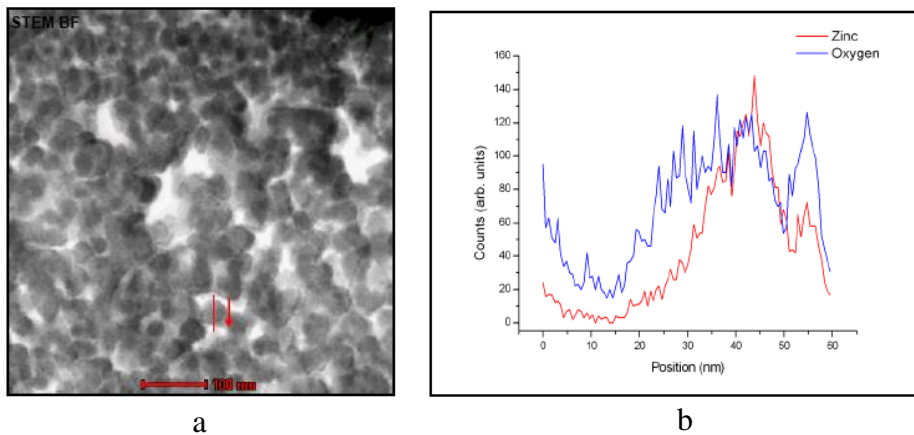


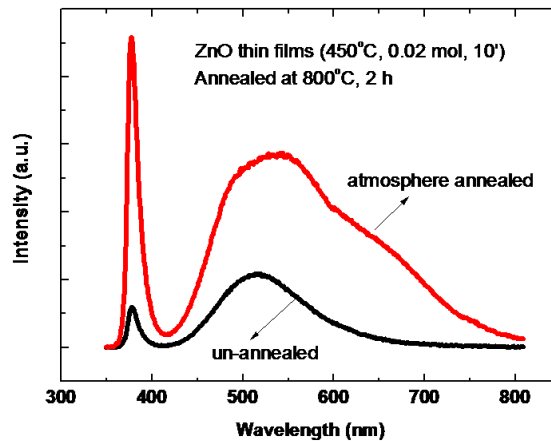
Figure 3. (a) Morphology of the ZnO film (b) E.D.X. Line scan taken from one particle of  $Zn_xO_y$

From Figure 3 b, It is seen that the concentration of Oxygen is higher than the concentration of Zn. It indicate the present of Zn Vacancy.

### 4.3 Photoluminescence (PL)

Photoluminescence is a process where a molecule absorbs a photon in the visible region. It is exciting one of its electrons to a higher electronic excited state, and then radiates a photon when the electron returns to a lower energy state. Photoluminescence spectroscopy is a technique for characterization of the optical and electronic properties of materials.

The room temperature PL for un-annealed and annealed of ZnO films is shown in Figure 2. It shows ZnO film properties which consists of narrow UV peaks at around ~380 nm and broad deep level peak at around 510-600 nm



**Figure 2 :** Room temperature PL spectra of non annealed and annealed at 800°C for 2 hours

The peak at around ~380 nm may due to free exciton recombination process which can be related to the interface traps that exist in the grain boundaries. The strong green band may be due to the presence of defect (deep level emission), appear as broad peak at around 510-600 nm.

The deep level emission might probably relative variations of the intrinsic defects in ZnO films [14,15,16]. These defects generally are zinc vacancy  $V_{Zn}$ , oxygen vacancy  $V_O$ , interstitial zinc  $Zn_i$ , interstitial oxygen  $O_i$ , and antisite oxygen  $O_{Zn}$  [Error! Bookmark not defined.].

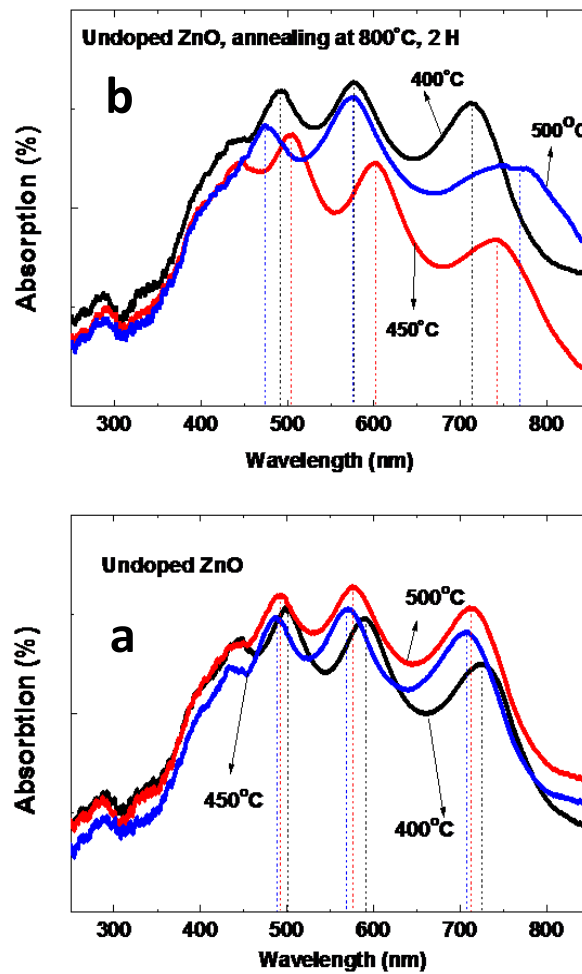
Sun had calculated energy level of ZnO tfilms by applying the full potential linear muffin-tin orbital method [Error! Bookmark not defined.,17]. Meanwhile, Fan found that the electron transitions from the bottom of the conduction band to the antisite oxygen  $O_{Zn}$  and the interstitial oxygen  $O_i$  defect levels should mainly contribute to the deep level emission of PL spectra of ZnO films [Error! Bookmark not defined.].

#### 4.4 Vis-NIR

Vis-NIR Spectroscopy is based on the absorption visible-NIR light by chemical compounds. The absorption spectra of undoped ZnO films at growth temperatures 400°C, 450°C, and 500°C, for non annealed, and annealed at 800°C for 2 hours are shown in Figure 3. Using Planck's equation  $E = hv$ , the absorption spectra peaks, the defect's energy level of ZnO films can be determined. The calculated energy interval of ZnO films grown by USP is relative to the electronics transition from the bottom of conduction band to the O vacancy ( $V_O$ ), O interstitial ( $O_i$ ), and antisite O ( $O_i$ ).

The defect's energy level of ZnO films grown by USP is shown on Table 1. It is shown that the defect's energy level varies non linearly for the samples non annealed and annealed for each growth temperatures.

The calculated energy interval of deep level emission is shown on Table 2. The Table 1 and Table2 show the defect's energy level of ZnO film growth at temperature 500°C with annealed 800°C for 2 hours coincide with the energy interval of deep level emission (1.62 eV). It might be attributed to the electronic energy transition from the bottom of conduction band to the oxygen vacancy ( $V_O$ ) energy level, 1.62 eV. It is common known that substrate Si is easy to be oxidized [18], so the interface layer  $SiO_2$  which is formed between Si and ZnO layer, is increase in oxygen vacancy ( $V_O$ ). Furthermore, by increasing oxygen vacancy  $V_O$  can suppress the concentraton amount of antisite oxygen in ZnO films [Error! Bookmark not defined.].



**Figure 3 :** Absorption spectra of undoped ZnO thin films at growth temperatures 400°C, 450°C, and 500°C, a) non annealed, b) annealed at 800°C for 2 hours

**Table 1:.** Defect’s energy level of ZnO thin films grown by USP

| No | 400 °C       |          | 450°C        |          | 500°C        |          |
|----|--------------|----------|--------------|----------|--------------|----------|
|    | E (eV)       |          |              |          |              |          |
|    | Non-Annealed | Annealed | Non-Annealed | Annealed | Non-Annealed | Annealed |
| 1  | 2.49         | 2.53     | 2.55         | 2.46     | 2.53         | 2.62     |
| 2  | 2.10         | 2.16     | 2.18         | 2.07     | 2.16         | 2.16     |
| 3  | 1.71         | 1.74     | 1.76         | 1.68     | 1.74         | 1.62     |

Meanwhile, the other defect’s energy level are not coincidence with the energy interval of deep level emission. It can be predicted that the defect’s energy interval between 2.16 up to 2.18 eV might be originate from oxygen interstitial ( $O_i$ ) and the defect’s energy level around 2.5 eV (2.46 up to 2.55 eV) might be originate from the electron energy transition from the level of the ionized oxygen vacancies to the valence band level [19]. Ionized vacancies is believed to be responsible for the green emission in ZnO films [20].

**Table 2 :** The energy interval of ZnO film deep level emission [14, 17]

| Defect's energy (eV) | Intrinsic defect |                 |
|----------------------|------------------|-----------------|
|                      | 1.62             | V <sub>o</sub>  |
| 2.28                 | O <sub>i</sub>   | O interstitial  |
| 2.38                 | O <sub>zn</sub>  | Anti site O     |
| 2.9                  | Zn <sub>i</sub>  | Zn Interstitial |

#### 4. CONCLUSION

The ZnO films have been coated on Si (111) substrate by ultrasonic spray pyrolysis (USP) at various growth temperatures 400°C, 450°C, and 500°C successfully. The annealed were performed for each ZnO films at temperature 800°C for 2 hours. The XRD spectra show that a ZnO thin film has polycrystalline structure. The ZnO films show a typical luminescence behaviour. The defect's energy level 1.62 eV should be attributed to the electronic transition from the bottom of conduction band to the oxygen vacancy (Vo). The defect's energy interval about 2.16 up to 2.18 eV originate from oxygen interstitial (Oi) and the defect's energy level about 2.5 eV (2.46 up to 2.55 eV) originate from the electron transition from the level of the ionized oxygen vacancies to the valence band.

#### 5. ACKNOWLEDGEMENT

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