Blueshift of the Optical Bandgap in ZnO Films by Controlling the Substrate Temperature

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Abstract: This study investigates the growth of ZnO thin films using the spray pyrolysis method, focusing on the effect of substrate temperature on the optical bandgap. By varying the deposition temperature from 300 to 500°C, we aim to understand how temperature influences the optical properties of ZnO films. The films were characterized using X-ray diffraction (XRD) and UV-visible spectroscopy (UV-Vis). At 300°C, the absorption was lowest, and the optical bandgap increased from 3.20 eV at 300°C to 3.70 eV at 500°C. These findings are crucial for developing ZnO materials for optoelectronic applications using an efficient and cost-effective deposition method.

Keywords: Optical bandgap; Optoelectronics; Spray pyrolysis; Thin films; Zinc oxide

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I. INTRODUCTION

Zinc oxide (ZnO) is a semiconductor with applications in gas sensors [1], photocatalysts [2, 3], ultraviolet detectors [4], and transparent conductors for photovoltaic devices and flat panel displays [5]. ZnO has a wide energy band gap (3.3 eV), large exciton binding energy (60 meV), non-toxicity, and high transparency in the visible spectrum making it highly promising for future optoelectronic devices. Enhancing ZnO functionality often involves atomic doping [6, 7].

Various deposition techniques, including chemical vapor deposition and physical vapor deposition (e.g., dc sputtering [7, 8], pulsed laser deposition [9], molecular beam epitaxy [10], and thermal evaporation [11]), have been used to grow ZnO films. However, these methods are costly due to the need for vacuum technology and high electricity usage. Solution-based techniques like chemical bath deposition [12], sol-gel [13], spin coating [14], dip coating [15], and spray pyrolysis [3] are more cost-effective and versatile. Spray pyrolysis, in particular, offers a fast and simple method to grow ZnO films with controlled particle size by adjusting the precursor concentration and deposition parameters [3].

On the other hand, spray pyrolysis was chosen to grow ZnO crystal films faster and simpler than other solution-based chemical techniques [16]. Our previous study showed that the required deposition time was less than 30 seconds with simple solvents (ethanol) [16]. However, investigations into the optical properties of ZnO grown by ultrafast spray pyrolysis have rarely been studied. It is important to note that rapid deposition can alter the optical spectrum of the ZnO film. Here, the ZnO films were deposited using an ultrafast spray technique with different growth temperatures. The effects of temperature on the optical band gap of ZnO are deeply investigated in this work.

II. EXPERIMENTAL METHODS

ZnO films were grown on soda lime glass substrates using the spray pyrolysis technique. The substrates were cleaned sequentially with acetone, ethanol, and aquadest, each for 5 minutes. A 0.4 M precursor solution was prepared by dissolving zinc acetate dehydrate ($Zn(CH_3CO_2)_2.2H_2O$) in ethanol (C_2H_6O). The solution was stirred at room temperature at 180 rpm for 60 minutes. The distance between the nozzle and substrate was maintained at $\sim$ 8 cm during the spray process, which was conducted for 30 seconds per film. The substrate temperature was varied from 300 to 500°C. A detailed experiment was reported elsewhere [17].

The crystal structure of the films was studied using a Bruker D8 Advance diffractometer with CuKα radiation (λ = 1.5418 $\mathring{A}$) and a step size of 0.02°. Diffuse reflectance spectroscopy was performed in the 200-900 nm range with a 0.5 nm interval to analyze the optical properties. This technique is effective for probing defect states in wide-bandgap semiconductors [18].

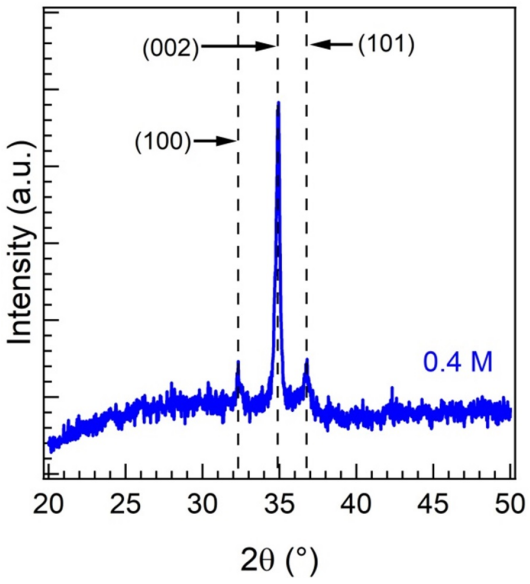

FIG. 1: XRD pattern of ZnO films grown at a substrate temperature of 450°C.

III. RESULTS AND DISCUSSION

Fig. 1 shows the XRD pattern of ZnO films grown at 450°C, indicating the presence of (100), (002), and (101) planes at 32.17°, 34.85°, and 36.72°, respectively, corresponding to the hexagonal wurtzite structure. The dominant (002) peak suggests c-axis orientation. The interplanar spacing (d), lattice parameters (a and c), crystallite size (D), and lattice strain (ϵ) were calculated using the following expression.

$$2d\ sin\ \theta = n\lambda \tag{1}$$

The lattice parameters of a and c are 3.21 and 5.14 $\mathring{A}$, respectively. ZnO semiconductor lattice parameters depend on (i) concentration free electrons, (ii) defects either intrinsic or extrinsic and their difference with radius ionic to the host material, (iii) external strain, and (iv) temperature. The full width at half maxima (β) of the (002) plane is 0.19°. The crystalline size (D) is 45 nm, and the lattice strain (ϵ) is 3×10^{-3}, as calculated by the following expression:

$$D = \frac{K\lambda}{\beta\ cos\ \theta} \tag{2}$$

$$\epsilon = \frac{\beta}{4\ tan\ \theta} \tag{3}$$

Kubelka-Munk's theory is usually used to analyze the diffuse reflectance spectra [19]. Fig. 2 shows diffuse reflectance spectra for ZnO film. Below the bandgap region (< 3.3 eV), the reflectance of the S500 sample is higher than the others. Above the bandgap region, the reflectance of the S300 sample is higher than the others. Absorption coefficient (α) is obtained from reflectance spectra using the Kubelka-Munk relation :

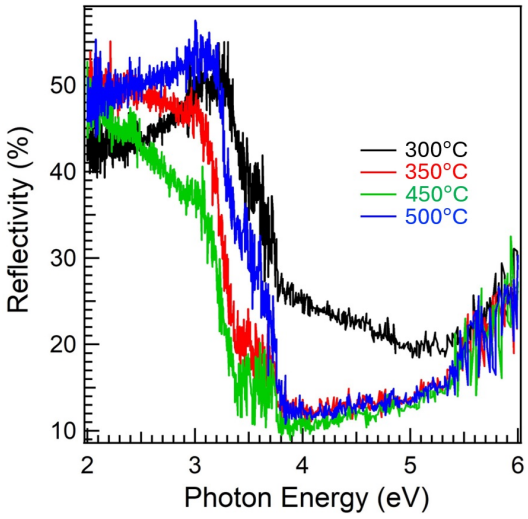

FIG. 2: Reflectivity spectra of ZnO films grown by ultrafast spray pyrolysis.

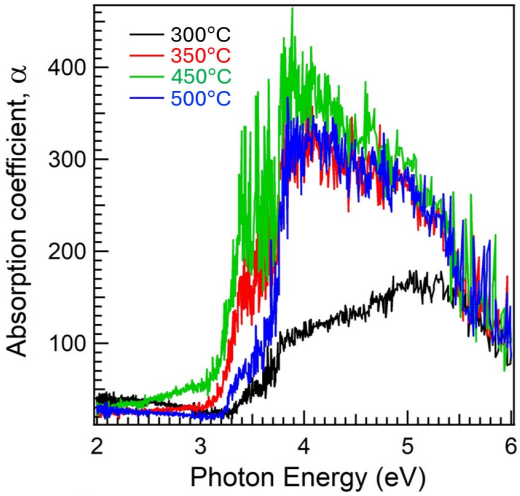

FIG. 3: Absorption coefficient (α) spectra of ZnO films for different growth temperatures.

$$F(R_\infty) = \frac{(1-R_\infty)^2}{2R_\infty} \tag{4}$$

where $F(R_\infty)$ is the Kubelka-Munk function. This function is proportional to the absorption coefficient (α)

$$F(R_\infty) \approx \alpha \approx \frac{(E-E_g)^n}{E} \tag{5}$$

where E is the photon energy and E_g is the optical bandgap. The absorption coefficient spectra are plotted in Fig. 3.

The optical bandgap of the film is estimated using the Tauc model in the high absorbance region [20]

$$\alpha E = A(E-E_g)^n \tag{6}$$

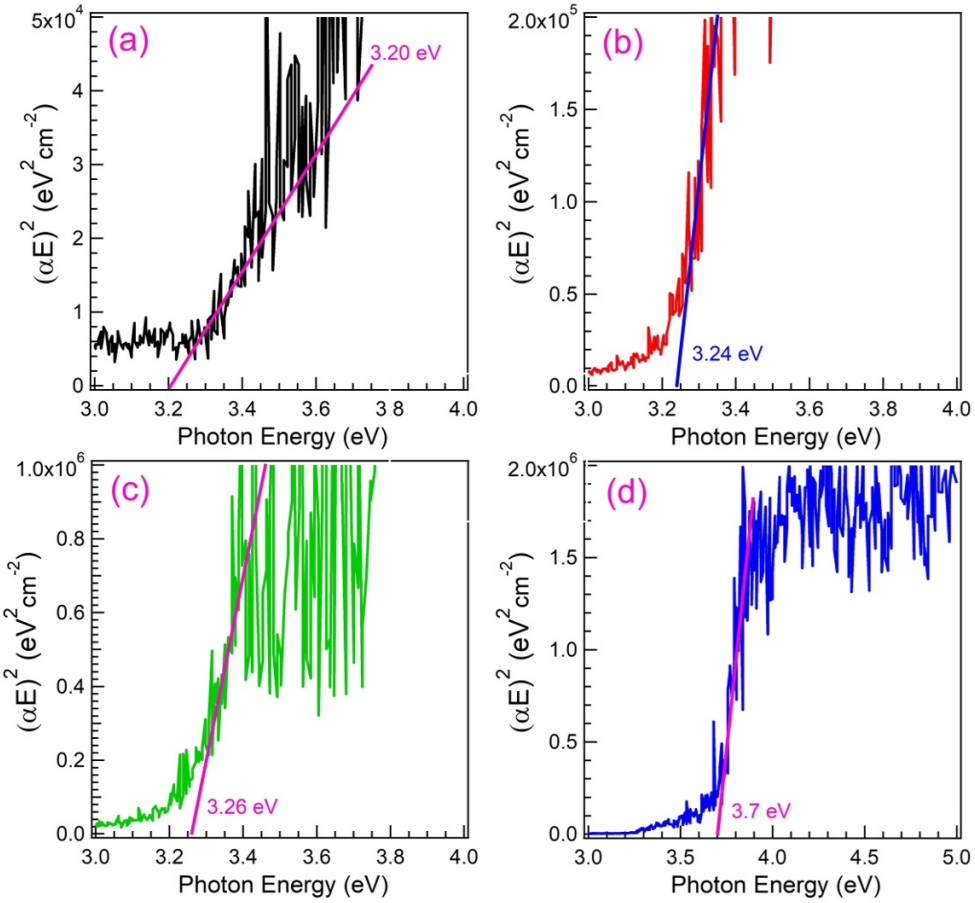

FIG. 4: Tauc-plot method of ZnO films for growth temperatures of (a) 300, (b) 350, (c) 450, and (d) 500°C.

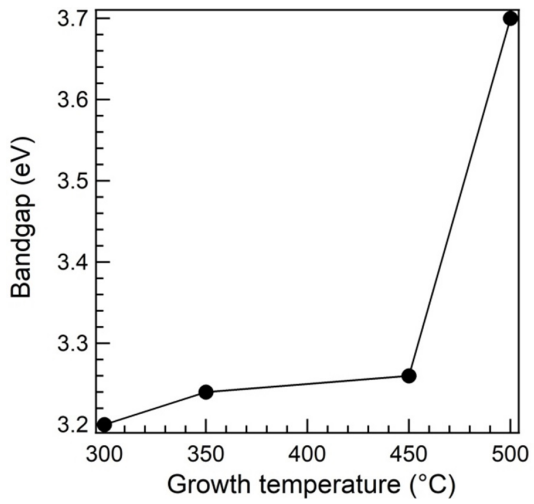

FIG. 5: Optical bandgap of ZnO films as the function of growth temperature.

For ZnO that have a direct transition, n = $\frac{1}{2}$ are used. This value is suitable since it gives a better linear curve in the band-edge region. For ZnO that have a direct transition, are used. This value is suitable since it gives a better linear curve in the band-edge region. Fig. 4 shows the relationship between $(\alpha E)^2$ and E. The bandgap can be obtained by linear extrapolation to the x-axis. The bandgap value is obtained at $y = 0$ (Fig. 4).

Fig. 5 shows the dependence of optical bandgap on growth temperature. The optical bandgap increased from 3.20 eV at 300°C to 3.70 eV at 500°C, consistent with previous studies that show temperature-induced bandgap widening [21, 22]. Hwang *et al.* showed that the bandgap could be altered by applying growth temperature from 30 to 500°C during sputtering deposition [22]. The increase of tensile stress follows the blueshift of the bandgap. The increase also follows this in carrier concentration and conductivity. However, Tan et al. showed that the blueshift of the ZnO bandgap (from 3.13 to 4.06 eV) was obtained by decreasing the growth temperature from 500 to 200°C [23]. The blueshift is generally caused by low crystallinity [23, 24].

In degenerate semiconductors such as ZnO, the bandgap is mainly influenced by the change in carrier concentration. The observed blueshift is attributed to the Burstein-Moss effect, where increased carrier concentration blocks lower energy states in the conduction band [25]. The narrowing effect may be associated with various many-body interactions

between carriers in the valence and conduction band. It is also called bandgap renormalization [25 - 27]. This tuneable bandgap of ZnO materials has the potential for optoelectronic applications.

IV. CONCLUSION

In conclusion, ZnO films were successfully fabricated using ultrafast spray pyrolysis at growth temperatures ranging from 300 to 500°C. The optical bandgap increased with temperature, demonstrating the potential for tuning ZnO properties for optoelectronic applications. This study highlights the effectiveness of ultrafast spray pyrolysis as a low-cost, efficient deposition method.

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