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Structural, morphological and optical studies of various substrate temperatures of ZnO thin films by spray pyrolysis

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Abstract
We report the synthesis and characterisation of *ZnO* by using Spray pyrolysis method. The synthesized *ZnO* thin films of various substrate temperatures (300 °C, 350 °C, 400 °C and 450 °C) have been characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), energy dispersive X-ray analysis (EDX), and UV-Visible spectroscopy. The crystal structures of *ZnO* have been confirmed with crystallite sizes 15.65nm-32.91 nm, the dislocation density, microstrain decreasesed, interplanar distance also decreased from 2.159 to 1.942 for 300 °C to 450 °C of substrate temperatures using XRD data. The nanoparticles (NPs) grain size increase from 48.3 nm to 151.8nm by increasing substrate temperature morphologies of *ZnO* have been observed by using FESEM. The elemental compositions have been investigated using EDX. The optical band gap for *ZnO* has been estimated that on increasing substrate temperatures (300 °C, 350 °C, 400 °C and 450 °C) is decreased (3.203eV to 3.045eV) from UV-Visible analysis data.

Keywords: Glass substrates, thin films, UV-absorption, XRD, ZnO

Introduction

The zinc oxide thin film is a semiconductor material, allowing for efficient electron transport within the solar cell. When photons from sunshine are absorbed by dye molecules on the thin film's surface, they produce excited electrons. To create electrical current, the electrons must be promptly transferred to the electrode. Zinc oxide, with its particular electronic characteristics, aids in the electron transfer process, assuring the effective conversion of light energy into electrical energy. Zinc oxide thin film is an important component of dye-sensitized solar cells. It functions as a semiconductor, allowing for efficient electron transport, provides a broad surface area for dye absorption, serves as a protective layer, and improves the stability and endurance of the solar cell. Heterostructure solar cells, which use a combination of large band gap metal oxide semiconductors as electrodes and narrow bandgap semiconducting materials as dye sensitizers [1], are now gaining popularity.

ZnO is a metal oxide semiconductor that has been researched for a variety of uses in dye-sensitized solar cells. Because of its high electrical conductivity, non-toxicity, and inexpensive cost, *ZnO* has emerged as one of the most adaptable semiconductors in solar cells [2-4]. *ZnO* is a wide band gap semiconductor with 3.37 eV that belongs to the II - VI group and has a high binding energy of around 60 meV. *ZnO* remains stable in severe environments [5]. *ZnO* has potential uses in a variety of sectors, including laser diodes [6-7], piezoelectric materials [8], gas sensors, and solar cells [9-10]. *ZnO* has numerous forms, including nanoflowers, nanoneedles, and nanorods [11].

Several experimental approaches have been documented in the literature, including chemical bath deposition (CBD) [12-13], electrodeposition [14-15], hydrothermal [16-17], and magnetron sputtering [18-19].Spray pyrolysis is the most extensively utilized of the technologies listed above due to its simplicity, cost-effectiveness, continuous operation, high deposition rate, and ability to deposit on large surfaces [20-23]. Controlling substrate temperature during deposition is critical for developing zinc oxide (*ZnO*) thin films for dye-sensitized solar cells (DSSCs). The substrate temperature can change the structural, optical, and electrical properties of the *ZnO* layer, impacting the solar cell's overall performance. The substrate temperature affects the optical transparency and bandgap of *ZnO* films. In order for DSSCs to absorb light and inject electrons efficiently, bandgaps must be transparent and well defined. Higher substrate temperatures during deposition can promote crystallization and improve the orientation of *ZnO* sheets. This can result in better charge transport characteristics and lower defect density, which is beneficial to DSSC performance.

In this study, *ZnO* thinfilms are formed at various substrate temperatures (300 °C, 350 °C, 400 °C and 450 °C) while maintaining a consistent flow rate and duration. The synthesized *ZnO* thinfilms of various substrate temperatures (300 °C, 350 °C, 400 °C and 450 °C) have been characterized by X-ray diffraction (XRD), Field emission scanning electron microscopy (FESEM), Energy dispersive X-ray analysis (EDX), and UV-Visible spectroscopy.

Materials and Methods

ZnO thinfilms are deposited on glass substrate of different temperatures using spray pyrolysis method [21-22]. A solution of 0.2M was prepared using concentration of zinc acetate dehydrate ($Zn(CH_3COO)_2.2H_2O$) precursor in 50 ml of deionized water (a drop of acetic acid is added to the solution to avoid precipitation of zinc hydroxide). The substrates were cleaned prior to deposition, first by soap water and then ultrasonically cleaned for about 24 min. Later dried in air for about 1 hour, the solution was sprayed with a solution spray rate of 1ml/min onto a preheated substrate at 300 °C during 15 min using compressed air as a carrier gas (The nozzle to substrate distance was about 25 cm). After deposition allowed to cool at room temperature then remove from apparatus, using same procedure for 350 °C, 400 °C and 450 °C with same distance, flow rate and time. In this study, we discussed about the effect of substrate temperature on structural, morphological, optical properties of the deposited *ZnO* thin films.

Results and Discussion

Structural Analysis

XRD measures the angles and intensities of diffracted X-rays to identify a material's crystal structure. The structural investigation of the *ZnO* thin films were performed by the X-ray diffraction (XRD). The XRD patterns were recorded by using an X-ray diffractometer with CuKα1 radiations (θ=1.5406 Å). The thin films grown in hexagonal wrutzite structure conformed by the JCPDS card no. 00-036-1451 the XRD peaks of *ZnO* thin films at 300 °C, 350 °C, 400 °C are observed at 31.9^0, 34.4^0, 36.3^0, 56.7^0, 72.6^0 respective hkl values are (100), (002), (101), (110), (004). But at 450 °C the dominant peak is (002).It is clear that (002) stronger while increasing temperature of substrates as shown in Fig. 1, similar findings were observed in the previous reports [24-25].

Lattice parameters, crystallite size, dislocation density, microstrain, d-spacing have been calculated using XRD patterns. Lattice parameters a, c are calculated using equation (1). It is observed that lattice parameters are slightly vary with increase of substrate temperature.

$$1/d^2 = 4/3((h^2+hk+k^2)/a^2) + l^2/c^2 \text{ - (Eqn. 1)}$$

Average crystallite size calculated from debye sherrer formula equation (2). Crrystallite size increases from 15nm to 32nm as increasing substrate temperature.

$$D=0.9\lambda/\beta \cos\theta \text{ - (Eqn. 2)}$$

Where D is crystallite size, λ is wavelength (1.5406A°) of X-rays used, β is full width half maxima in radians, θ is angle of diffraction in radians. The dislocation density, microstrain, interplanar distance are determined using equation (3), (4), (5) respectively. Those are decreases with increasing substrate temperature similarly reported [21]. Those are tabulated in Table. 1.

$$\theta 1/D^2 \text{ (lines/m}^2\text{) - (Eqn. 3)}$$

Where D is grain size

$$\varepsilon=\beta/4\tan\theta \text{ - (Eqn. 4)}$$

$$d=\lambda/2\sin\theta \text{ - (Eqn. 5).}$$

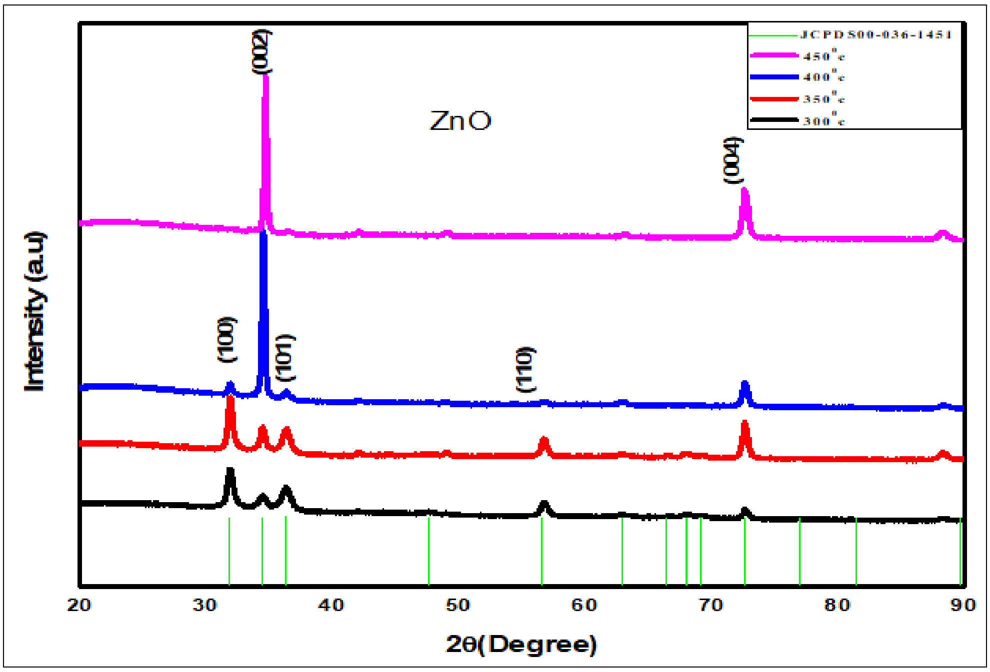

Fig 1: XRD patterns of *ZnO* films deposited at 300 °C, 350 °C, 400 °C and 450 °C

Table 1: Calculated values of *ZnO* thin films deposited at different temperatures

Sample details	Lattice parameters		Crystallite size(D)nm	Dislocation density(d)	Microstrain (Ɛ)	D spacing
	A	C				
Standard	3.2498	5.2066				
300°C	3.2363	5.1996	15.65	4.93	7.2	2.159
350 °C	3.2474	5.2177	19.16	3.38	5.81	2.166
400 °C	3.2377	5.1901	24.6	2.17	4.37	2.158
450 °C	----	5.1669	32.91	1.37	2.8	1.942

Morphological Analysis and EDS

The surface morphology analysis of films studied by field emission scanning electron microscope. Fig. 2 illustrates that the grain size increases that is at 300 °C, 350 °C, 400 °C and 450 °C grain sizes are 48.3 nm, 79.2 nm, 89.5 nm, 151.8 nm with increasing substrate temperature of *ZnO* thin films calculated by using imageJ software. Nanospheres are observed from Field emission scanning electron microscope. Previous reports [26-27] demonstrated nanospheres and nanorods with increasing grain size.

The elemental composition studied by energy dispersion spectroscopy as shown in Fig. 3. Zinc weight percentage increases upto 400 °C then decrease at 450 °C and oxygen weight percentage decreases upto 400 °C then increase at 450 °C shown in Table. 2. Here we observed that zinc percentage increased and oxygen percentage decreased. silicon, calcium, aluminium, magnisium, sodium, carbon elements are observed in 300 °C, 350 °C and 450 °C whereas 400 °C silicon, carbon, calcium are observed elements. These elements are due to glass substrate we used.

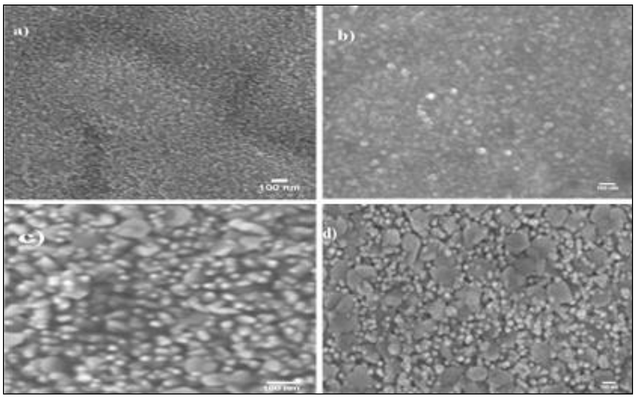

Fig 2: FESEM of *ZnO* films deposited at a) 300 °C, b) 350 °C, c) 400 °C, d) 450 °C

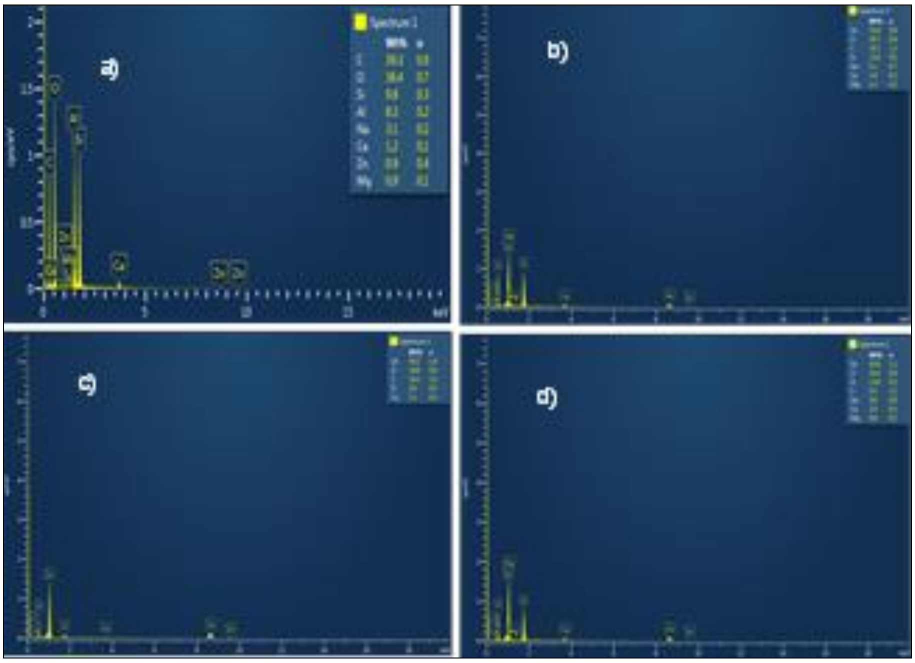

Fig 3: (a), (b), (c), (d) Energy Dispersion Spectroscopy for *ZnO* deposited at 300 °C, 350 °C, 400 °C and 450 °C

Table 2: Elemental composition of *ZnO* films at 300°C, 350 °C, 400 °C and 450 °C

Film sample	Elements	Weight%	Atomic%
300 °C	Zn	0.9	0.4
	O	36.4	0.7
350 °C	Zn	33.6	0.9
	O	26.7	0.8
400 °C	Zn	59.2	1.4
	O	18.8	0.9
450 °C	Zn	42.8	1.1
	O	24.5	0.8

Optical analysis

The optical properties are studied by UV-VIS spectroscopy. From UV absorption data calculated absorption, transmittance, bandgap from Tauc relation at different substrate temperatures 300 °C to 450 °C of *ZnO* films as shown in Fig. 4 to 6. The wavelength range taking from 350 nm to 800 nm for absorbance, transmittance graphs. The absorption edge at 388nm blue shift (moving away from visible region) occurs as increase substrate temperature of *ZnO* films [27] The blueshift of absorption at the beginning of *ZnO* films absorption is related to the increase in charge carriers concentration, which blocks the lowest states of the conduction band (Burstein-moss effect).

The average transmittance at 80% and red shift (moving towards the visible region) occurs at substrate temperatures

300 °C, 350 °C, 400 °C, 450 °C of *ZnO* films.

The relation between absorbance and transmittance from beer lambert's law $A=-\log_{10}(\%T)$

For optical bandgap Tauc relation calculated as follows.

From absorbance data calculate absorption coefficient $\alpha=2.303*A/t$

Where 'A' is Absorbance, 't'is thickness of film

Energy E in eV=1240/λ

Where λ is wave length in nano meters

Then we plotted graph $(\alpha h\nu)^2$ vs $h\nu$ at different substrate temperatures of *ZnO* films. The bandgaps are 3.203 eV, 3.188eV, 3.086 eV, 3.045 eV at 300 °C, 350 °C, 400 °C and 450 °C respectively. As bandgap decrease with increase grain size at different substrate temperatures of *ZnO* films, previous report [28] suggested dye sensitised solar cell band gap decreased. In our work the bandgap decreased while increasing substrate temaperature. It is applicable for Dye sensitised solarcell.

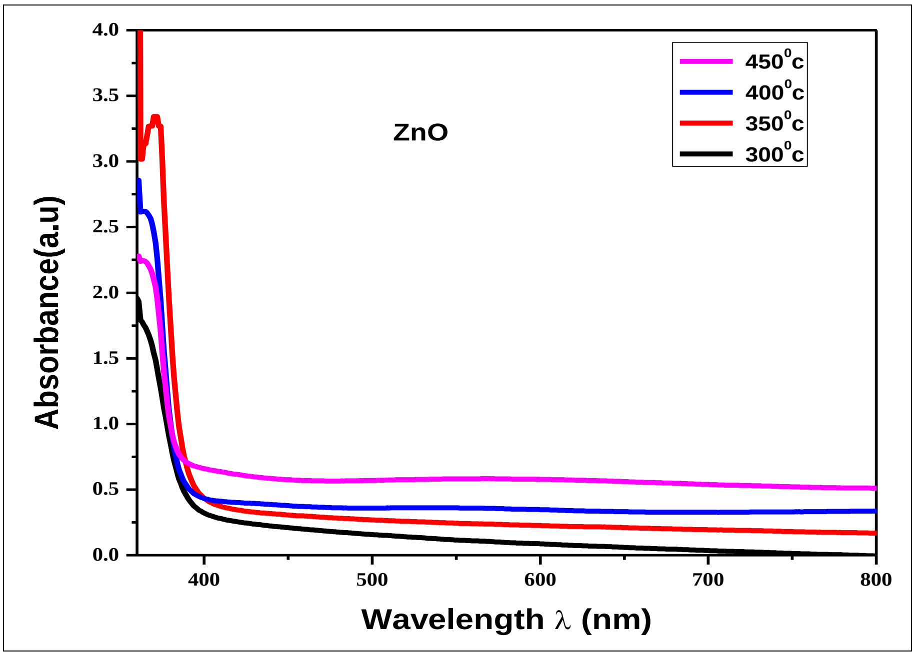

Fig 4: Optical absorbance of *ZnO* films at 300 °C, 350 °C, 400 °C and 450°C

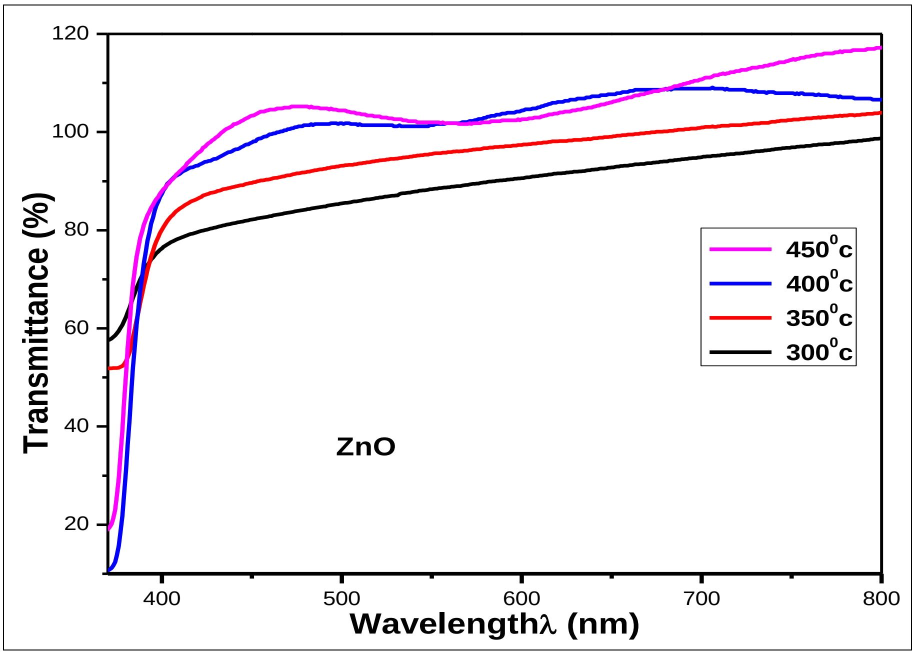

Fig 5: Optical transmittance of *ZnO* films at 300 °C, 350 °C, 400 °C and 450 °C

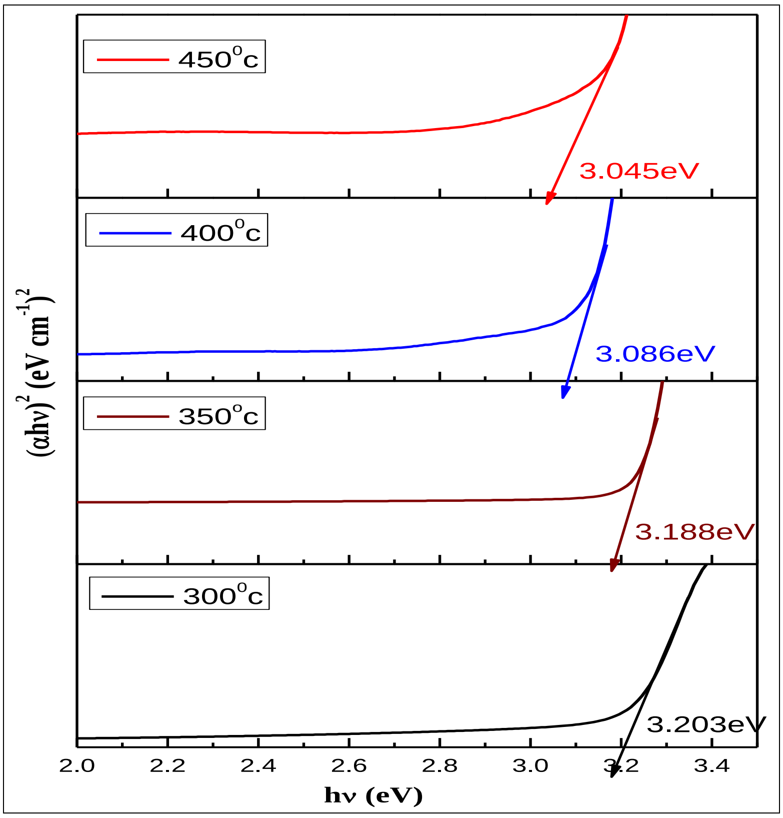

Fig 6: Optical bandgap of *ZnO* films at 300 °C, 350 °C, 400 °C and 450 °C

Conclusion

In this study, the results of *ZnO* films deposited at different substrate temperatures (300 °C to 450 °C) on glass substrates by Spray Pyrolysis technique studied. From XRD analysis confirmed that crystal size increases from 15.65nm to 32.91 nm calculated from debye sherrer formula, d-spacing varies, dislocation density and microstrain decreases as increase substrate temperatures. It is confirmed that (002) is preferred orientation with hexagonal wrutzite structure. From FESEM it is cleared that grain size increases from 48.3nm to 150 nm. From EDS confirmed that elemental compositions are increased while increasing substrate temperature. From UV-VIS spectroscopy the absorption decreases, transmittance increases, bandgap also increases from 3.17eV to3.26eV as increase substrate temperatures of *ZnO* films. Finally, we concluded that the *ZnO* thinfilms crystal size, bandgap increased as increase in substrate temperature.

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Conflicts of Interest

The authors declare no conflict of interest.

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