Photovoltaic Properties of Co-doped ZnO Thin Film on Glass Substrate

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***Abstract*— Cobalt (Co) 0.4 mol doped zinc oxide (ZnO) fine powder was prepared by solid state mixed oxide route. Phase formation and crystal structure of Co-doped ZnO (CZO) powder were examined by X-ray diffraction (XRD). Scanning Electron Microscopy (SEM) was used to observe the micro structure of Co doped ZnO powder. Energy Dispersive X-ray Fluorescent (EDXRF) technique gave the elemental content of cobalt and zinc. Co-doped ZnO film was formed on glass substrate by spin coating technique. Photovoltaic properties of CZO/glass cell were measured.**

***Keywords*—Co-doped ZnO, XRD, SEM, spin coating**

I. INTRODUCTION

Zinc oxide (ZnO) is a unique material with direct band gap(3.37eV) and large excitation energy of 60 meV. It has been widely used in near-UV emission, gas sensor, transparent-conductor and piezoelectric application. Most of the ZnO crystals has been synthesized by traditional high temperature solid state method which is energy consuming and difficult to control the particle properties [1]. ZnO thin film is one of the II-VI compound semiconductors and is composed of hexagonal wurtzite crystal structure. ZnO thin film presents investigating optical, acoustical and electrical properties which meet extent applications in the field of electronics, optoelectronics and sensor. ZnO thin film is applied to the transparent conductive film and the solar cell window because of the high optical transmittance in the visible region [2]. Cobalt doped ZnO, among varity of applications, has been attracted due to intense green color, and it can be used as medium pigment. However, Lavat et al showed good blue pigments for ceramic industry [3].In this work, Co-doped ZnO thin films have been deposited by spin coating method. Co doped ZnO fine powder was prepared by solid state mixed oxide route. Microstructure and morphology of CZO powder and film were characterized by using XRD and SEM. Electrical properties of CZO film by I-V measurement under illumination were investigated.

II. EXPERIMENTAL PROCEDURE

The starting materials were CoO and ZnO. These samples were weighed by digital balance. Firstly, each powder were grounded by agate motor for 3h to obtain the homogenous and uniform grain size and shown in Fig 1.

Fig 1 Agate motor

And then mesh sieving method was used. Three stages mesh in the ascending order (100, 250 and 400) was used to get uniform grain size or particle size and mesh sieve was shown in Fig 2.

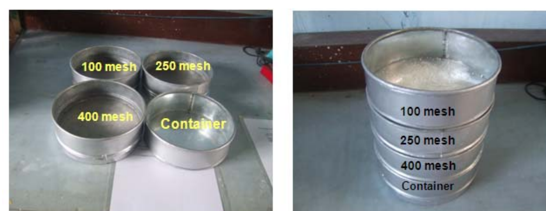

Fig 2 Three-stage mesh sieves

The last sieve with its retained powder was calculated.

Calculation

Total mass = 41.12g

Mass retained on a pan = 5.33g

Quantity passing = Total mass- Mass retained
= 35.79g

$$\% \text{ mass retained} = \frac{\text{mass retained}}{\text{total mass}} \times 100\ \%$$
= 12.96%

% passing = 100% - 12.96%
= 87.04%

Then, to get uniform and lightest particles the powder was stirred with the electric blender and shown in Fig 3.

Fig 3 Electric mixture

CZO powder was applied by ball milling method. The milling time interval was set for 20h. Sample was milled in grinding bowl (volume of 100g) with grinding balls (20 balls, 5mm diameter) at 800 rpm in air. Ball milling machine was shown in Fig 4.

Fig 4 Ball-milling machine

After ball milling, the sample was annealed in an oven at 300°C, 400°Cand 500°C for 1 h respectively. Block diagram for the preparation of homogenous CZO was shown in Fig 5. Then, the formation of the mixture was checked by X-ray diffraction (XRD) method, Scanning electron microscopy (SEM) and energy dispersive X ray fluorescence (EDXRF). The mixture powder were added with 2-Methoxyethanol ($CH_3O.CH_2.CH_2OH$) to maintain at 0.1M and stirred with magnetic stirrer at 50°C for lh. Then the mixture was refluxed to get the sol solution state with the oil bath at 110°C for 3h.

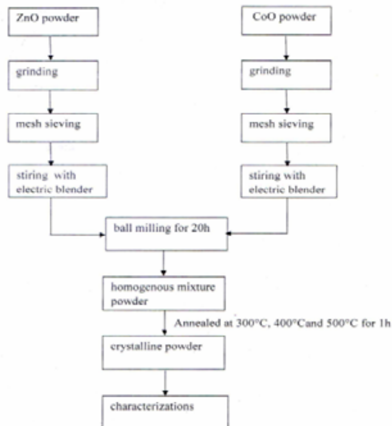

Fig 5 Block diagram for the preparation of homogeneous CZO

A. Substrates preparation

The glass (1cm ×1cm) wafer was used as a substrate. The glass surfaces can be effectively cleaned with soapy water. And it was immersed into the acetone about 5 min and then rinsed with distilled water and dry at room temperature. Firstly, surface of the glass was identified with LCR digital meter. The large conductivity side of the glass was coated with CZO sol solution by spin coating technique.

B. Thin film Deposition with Spin coating technique

The CZO sol solution was deposited on the glass substrates by Single Wafer Spin Processor. Single Wafer Spin processor was shown in Fig 6. The substrate was placed on Fragment Adapter and the CZO sol solution was dropped onto glass substrate. The rotational speed was 5000 rpm and spinning time was 30 sec. They were annealed at 400°C for 30 min and 1h respectively. Eventually, CZO/glass cells were formed at different temperatures. Fig 7 illustrates the flow chart which was showing the procedure for preparing CZO thin films. These films were determined by X-ray diffraction analysis (XRD) and scanning electron microscopy (SEM).

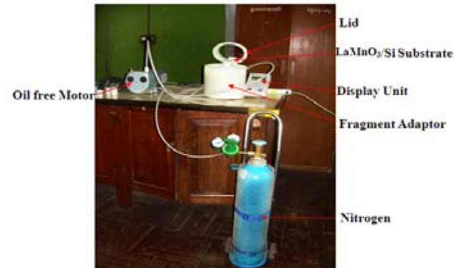

Fig 6 The photograph of spin coating system of the spin processor (MODEL WS-400BZ- 6N PP/LITE)

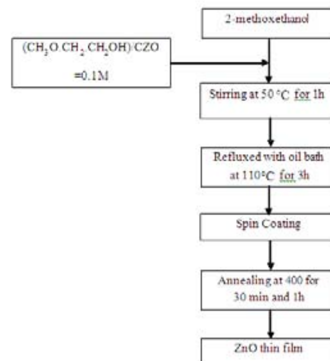

Fig 7 Block Diagram of the procedure for preparing CZO thin film

III RESULTS AND DISCUSSION

A. XRD Analysis

Structural analysis of the Co- doped ZnO powder was carried out using X- ray diffraction. X- ray diffraction, XRD is a non-destructive technique for the qualitative and quantitative analysis of the crystalline materials of the powder

or solid. The information about the crystallographic properties such as crystallite size and lattice parameters of all the samples has been obtained from the XRD profiles. Fig 8 (a-c) shown the X- ray diffraction patterns of Co- doped zinc oxide powder annealed at 300°C, 400°C and 500°C respectively. The characteristics peaks corresponding to the planes (100), (002), (101), (110), (103), (112) with high intensities and (102), (200), (201) low intense planes of the hexagonal ZnO wurtzite structure were displayed according to JCPDF file. The lattice distortion (or) lattice strain peaks after annealing at 400°C indicates the good crystalline nature of the powder improved through heat treatment.

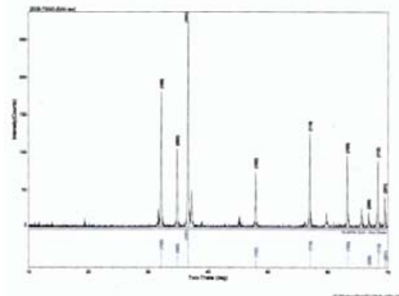

Fig 8 (a) X-ray diffraction patterns of Co doped ZnO powder annealed at 300°C

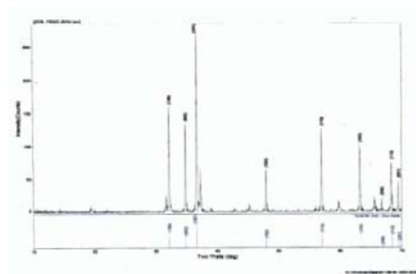

Fig 8 (b) X-ray diffraction patterns of Co doped ZnO powder annealed at 400°C

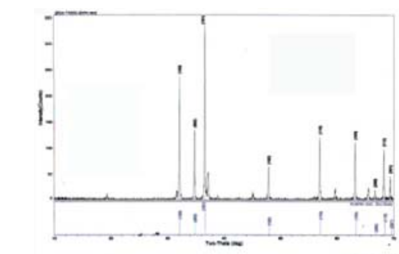

Fig 8 (c) X-ray diffraction patterns of Co doped ZnO powder annealed at 500°C

The crystallite grain size G of the powder was estimated by the Debye- Scherrer equation using the FWHM values obtained from the XRD data.

$$G = \frac{\beta\lambda}{FWHM \cos\theta} \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where

β = Scherrer constant ≅ 0.899
G = crystallite size (nm)
λ = wavelength ((λ = 1.5406 Å)
FWHM= full width at half maximum (rad)
Θ = Bragg angle (deg)

The lattice parameters a and c of the samples should be calculated using the formula.

$$\sin^2\theta = \frac{\lambda^2}{4}\left[\frac{4}{3}\left(\frac{h^2\text{-}hk\text{-}k^2}{a^2}\right)+\frac{l^2}{c^2}\right] \quad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

where

Θ = diffraction angle (deg)
λ = wavelength (λ = 1.5406 Å)
h,k,l = Miller`s indices

The calculated bond length (BL) and lattice distortion (c/a) were listed in Table 1.

TABLE I
BOND LENGTH AND LATTICE DISTORTION AT DIFFERENT TEMPERATURES

Temperature (°C)	B L (Å)	(c/a)
300	1.958	1.614
400	1.961	1.611
500	1.959	1.611

Lattice parameters of a-axis and c-axis, particle size (G) and the interplanar spacing (d) were also calculated and listed in Table 2.

TABLE II
LATTICE PARAMETERS, PARTICLES SIZE AND THE INTERPLANAR SPACING OF OBSERVED CO DOPED ZNO SAMPLE

Temperature (°C)	Lattice parametres (Å)		Crystallite size(nm)	d-spacing(Å) (101)
	a	c		
300	3.210	5.181	67.0	2.448
400	3.218	5.182	72.6	2.453
500	3.213	5.176	72.1	2.448

Lattice parameters and lattice distortion of standard ZnO powder were listed in Table 3.

TABLE III
LATTICE PARAMETERS AND LATTICE DISTORTION OF STANDARD ZNO POWDER

Lattice parameters (Å)		Lattice distortions (Å)
a	c	(c/a)
3.25	5.2	1.633

B. SEM Analysis

The morphology of the powder was investigated using the JEOL JSM-5610 LV scanning electron microscope. Fig 9 (a-c) showed the micrographs of the cobalt doped zinc oxide powder annealed at 300°C, 400°C and 500°C respectively. The surfaces were seen to be crack free and uniformly

distributed. Observation showed a homogeneous micro-structure formed by small grains of spherical shapes. The average grain size of the samples treated at 300°C was about 572 nm and the samples at 500°C was about 471 nm whereas it decreased to about 386 nm at 400°C (listed in Table 4). Based on these results, it was concluded that the average grain size of the powder varied with varying temperature.

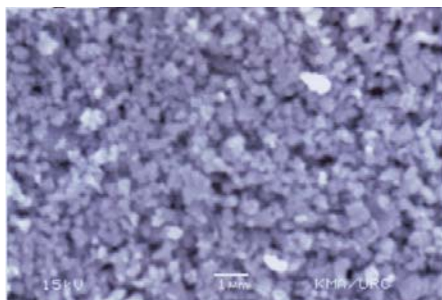

Fig 9 (a) SEM micrograph of the CZO powder annealed at 300ºC

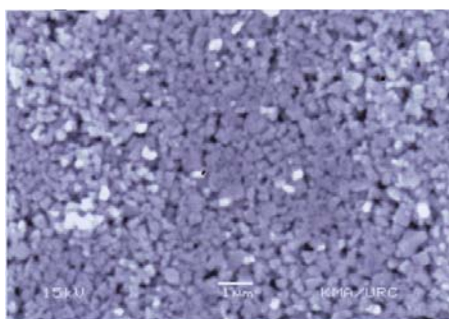

Fig 9 (b) SEM micrograph of the CZO powder annealed at 400ºC

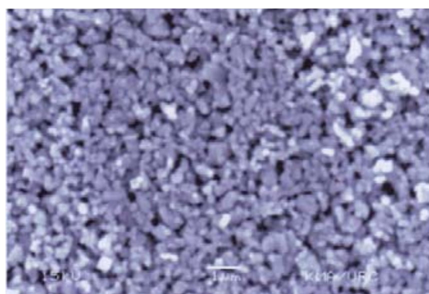

Fig 9(c) SEM micrograph of the CZO powder annealed at 500ºC

TABLE IV
THE VARIATION OF THE GRAIN SIZE WITH ANNEALING TEMPERATURE

Temperature (°C)	Grain size (nm)
300	572
400	386
500	471

C. EDXRF Analysis

Elemental contents of CZO powder was examined by EDXRF technique. Fig 10 (a-c) showed the XRF spectrum of CZO powder at different temperature at 300°C, 400°C and 500°C. Table 5 showed the quantitative of CZO powder.

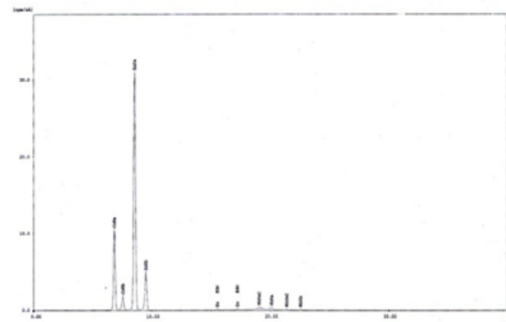

Fig 10 (a) XRF spectrum of CZO powder annealed at 300ºC

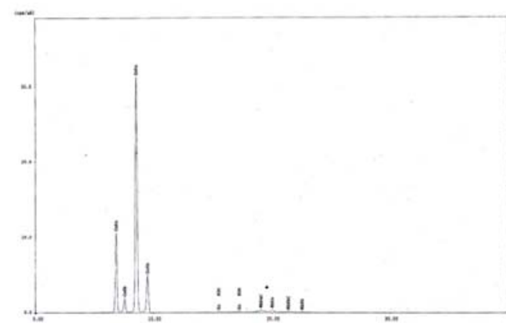

Fig 10 (b) XRF spectrum of CZO powder annealed at 400ºC

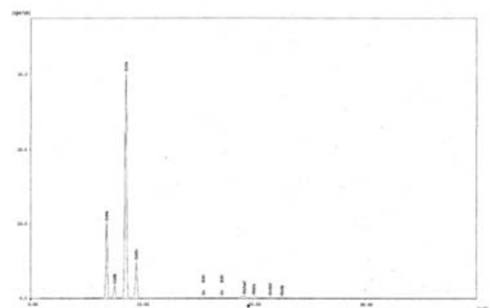

Fig 10 (c) XRF spectrum of CZO powder annealed at 500ºC

TABLE V
THE QUANTITATIVE ANALYSIS OF CZO POWDER

Temperature (°C)	Elemental concentration (%)	
	Zn	Co
300	83.862	16.138
400	83.997	16.003
500	84.093	15.907

E. Film Analysis by XRD

Fig. 11 (a & b) described the XRD profile of CZO film at 400 ºC for 30 min and 1h. From the result, the peak (101) was rather sharp, which indicated the obtained CZO film had relatively crystallinity and attributed to the polycrystalline nature. The crystallite size was estimated from the line broadening of X-ray diffraction using Scherrer formula. XRD diffraction peaks belonging to (100), (002), (102), (110), (103), (200), (112) and (201) planes were observed in all the CZO films. Compared to powder diffraction pattern of CZO structure, it was notice that lattice parameters were slightly decreased. Lattice parameters, particle size and the interplanar spacing of CZO film was listed in table 6.

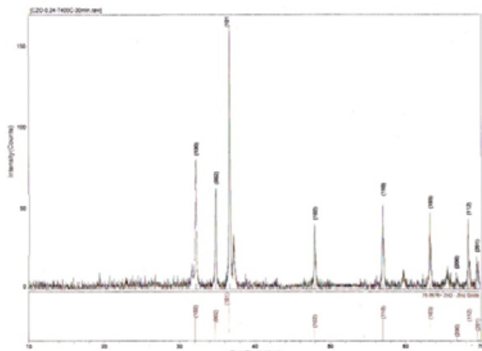

Fig 11(a) XRD pattern of CZO film at 400°C for 0.5 h

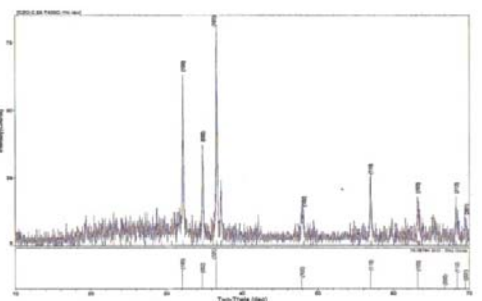

Fig 11(b) XRD pattern of CZO film at 400°C for 1.0 h

TABLE VI
LATTICE PARAMETERS, PARTICLE SIZE AND THE INTERPLANAR, SPACING OF CZO FILM

Temperature (400°C)	Lattice Parameters (Å)		crystallite size (nm)	d-spacing (Å)
	a	c		(101)
0.5 h	3.2136	5.1775	79.0	2.449
1.0 h	3.2139	5.1741	68.7	2.450

Table 7 showed the lattice parameters of CZO presented by Elilarassi R et al 2011. Concerning with the Table 6 and 7 the observed lattice parameters were found to be little difference in those of Elilarassi R et al 2011 [5].

TABLE VII
LATTICE PARAMETERS, PARTICLES SIZE AND THE INTERPLANAR SPACING OF ELILARASSI R ET AL 2011 CO- DOPED ZNO SAMPLE

Temperature (°C)	Lattice parameters (Å)		Crystallite size(nm)	d-spacing(Å)	
	a	c		(100)	(002)
300	3.252	5.206	33	2.8195	2.606
500	3.252	5.205	38	2.8179	2.605

F. Surface Morphology of CZO Thin Film

The CZO thin film surface morphologies were studied using scanning electron microscope (SEM). The SEM image of CZO film at 400°C for 30 min and 1 h were shown in Fig 12 (a&b). The surfaces were seem to be uniform distribution. The average grain size at 400°C for ½ h was 271.42 nm and for 1 h was 364.28 nm and listed in Table 8.

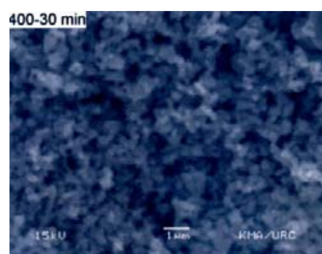

Fig 12(a) SEM micrograph of the CZO film annealed at 400°C for 0.5 h

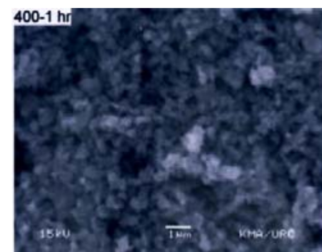

Fig 12(b) SEM micrograph of the CZO film annealed at 400°C for 1.0 h

TABLE VIII
THE GRAIN SIZE OF CZO FILM ANNEALING WITH DIFFERENT TIME

Temperature (°C)	Time (h)	Grain size (nm)
400	0.5	271.42
400	1.0	364.28

G. I-V measurement under illumination

The current-voltage characteristics of CZO thin films with different annealing temperature were illuminated under monochromatic Na-lamp of 5000 lux were represented in Fig 13. According to this figure, it was found that the current started from third quadrant increased gradually through the

fourth quadrant and finally reached into the first quadrant of the circle. As the detail analysis of short circuit current (I_{sc}), open circuit voltage (V_{oc}), maximum current (I_m) and voltage (V_m), conversion efficiency (η_{con})and fill factor (F_f) of the CZO cell at different temperature were shown in Table 9.

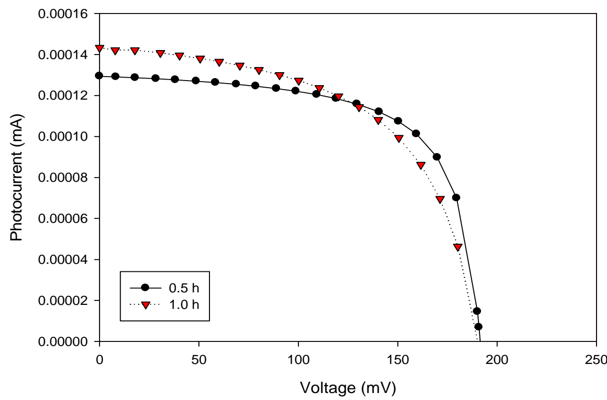

Fig 13. I-V measurement under illumination

TABLE XI
SOLAR CELL PARAMETERS OF CZO THIN FILM

Time of annealing temperature	**1.0 h**	**0.5 h**
I_{sc} (mA)	1.29 E -4	1.43 E -4
V_{oc} (mV)	191.15	190.1
I_m (mA)	1.06 E -4	1.09 E -4
V_m (mV)	152.1	138.05
η_{con} (%)	2.48	2.31
F_f	0.66	0.55

IV. CONCLUSION

The structural and electrical properties of Co doped ZnO thin films have been investigated. The XRD analysis of the CZO films confined the formation of a hexagonal wurtzite structure and good crystalline nature after thermal treatment. SEM images showed the formation of spherical microstructural particles. EDXRF spectrum gave the elemental content of Zn, Co and O in this sample and confirmed the presence of Co in the ZnO particles. It can be studied that technical simplicity and its easy adaptability. The conversion efficiency and fill factor of CZO cell were found to be 2.48, 2.31 and 0.66, 0.55 at different conditions. Thus CZO thin film was quite promising candidate for photovoltaic cell application.

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