Effect of Substrate on Structural, Optical and Electrical Properties of Zinc Oxide Thin Films Grown By Chemical Bath Deposition Technique

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Abstract:

This paper studied effect of substrate on the growth of zinc oxide thin films. Zinc oxide thin films were deposited on amorphous (glass) and indium tin oxide ITO substrate by using simple chemical bath deposition technique. The film deposited on ITO substrate has less resistivity than the film deposited on glass substrates. The films were analyzed with X-ray diffraction (XRD), Field emission scanning electron microscope (FESEM), Energy dispersive X-ray diffraction spectroscopy, UV-visible spectroscopy. X-ray diffraction studies reveal that films deposited on glass and ITO substrates are crystalline with a hexagonal wurtzite structure with a preferential orientation along (002) plane. FESEM image reveals that films deposited on ITO substrates have a uniformly distributed nanorods structure and are crack free. Energy dispersive spectroscopy (EDX) results indicate that Zn and O elements are present in the ZnO thin films deposited on glass and ITO substrate. Optical studies showed that slightly shifts the absorption edge of the films deposited on ITO substrates than film deposited on glass substrate.

Keywords: Thin film, chemical bath deposition, etc.

1. Introduction

Zinc oxide (ZnO) is one of the most promising materials because of its low cost, radiation hardness, high optical absorption in UV range, non-toxicity, high-temperature operation capability, environmental compatibility, high transparency, chemical stability, and a low resistivity [1-2]. The ZnO has large bandgap energy of 3.37eV and exciton binding energy of 60 meV [3]. The nanorods of ZnO have the significant benefit of a large surface-to-volume ratio hence they useful for capable of fabricating electronic and optoelectronic devices such as solar cell, ultraviolet photo-detector, gas sensors, photo-electrochemical (PEC) cell, photocatalytic and biological sensors, thin film transistors, LED (light emitting diodes), surface acoustic wave, and energy harvesting devices [4-8].

Growth of ZnOnanorods can be achieved by different deposition techniques such as successive ionic layer adsorption and reaction (SILAR) method [9], RF magnetron sputtering [10], reactive sputtering [11], molecular beam epitaxy (MBE) [12], pulsed laser deposition (PLD) [13] etc. Among these methods, chemical bath deposition technique is used to deposit ZnO thin film because of simple, low cost and does not need sophisticated instrumentation. It is applicable for large area deposition and uses a variety of conducting and non-conducting substrates. The structure, morphology, optoelectronic and photocatalytic properties of ZnO thin film can be controlled by changing the concentration of zinc precursor, pH of the solution and thickness of the film.

In this paper we study the effect on structural and morphological properties of zinc oxide thin films on glass and ITO substrates.

2. Experimental details

Chemicals used for the synthesis of ZnO thin film are as follows: AR grade of zinc sulfate heptahydrate ($ZnSO_4.7H_2O$), AR grade of thiourea (CH_4N_2S) and ammonia solution. De-ionized water was used to make the stock solution.

Synthesis of zinc oxide thin films on a glass and ITO substrates was carried out by the chemical bath deposition method. In the synthesis of ZnO, firstly 10 ml, 0.15M of zinc sulfate

solution was taken in a 50 ml glass beaker. Under continuous stirring 2.5 ml, 0.6 M thiourea solution was added slowly. Initially, the solution was milky turbid due to the formation of zinc-thiourea complex. After completing the reaction between thiourea and zinc ions, the ammonia solution was added to it slowly under continuous stirring. Addition of excess ammonia solution led to the dissolution of turbidity and made the solution clear and transparent. Then 17 ml of de-ionized water was added to make the final solution volume of 50 ml. The pH of the final bath solution was about 9.5. Pre-cleaned glass and ITO substrates were immersed and kept vertical in the beaker. The beaker was kept in constant temperature water bath and the bath was allowed to stand for 30 minutes at 80^{o}C temperature. Thereafter substrates coated with ZnO were removed, rinsed with de-ionized water and allowed air drying. The white color uniform films were obtained. Then, prepared films were annealed at 400°C in a muffle furnace for one hour.

The crystallite size, interlinear spacing, lattice constant, dislocation density has been determined from the obtained XRD data. The thickness has been measuredusing weight difference method. The absorbance data have been obtained from UV-Vis spectroscopy in the wavelength range 200 nm–800 nm.

3. Results and Discussion

3.1 Structural Properties

The crystal phases and structures of the ZnO thin films were performed using X-ray diffraction. The diffraction angle was varied from 20^{o} to 80^{o}. XRD pattern of ZnO thin film deposited on glass and ITO substrate was shown in Fig. 1 (a) and (b). XRD pattern of ZnO film deposited on a glass substrate was observed at 31.79^{o}, 34.46^{o}, 36.29^{o}, 47.60^{o}, 56.53^{o}, 62.90^{o} and 68.12^{o} corresponding to (100), (002), (101), (102), (110), (103) and (201) planes respectively, which belongs to hexagonal crystal structure with lattice parameters of a= 0.3247 nm and c= 0.5201 nm and coincide the peak with JCPDSdata(JCPDS80-0075, a= 0.3253 nm and c= 0.5209 nm).

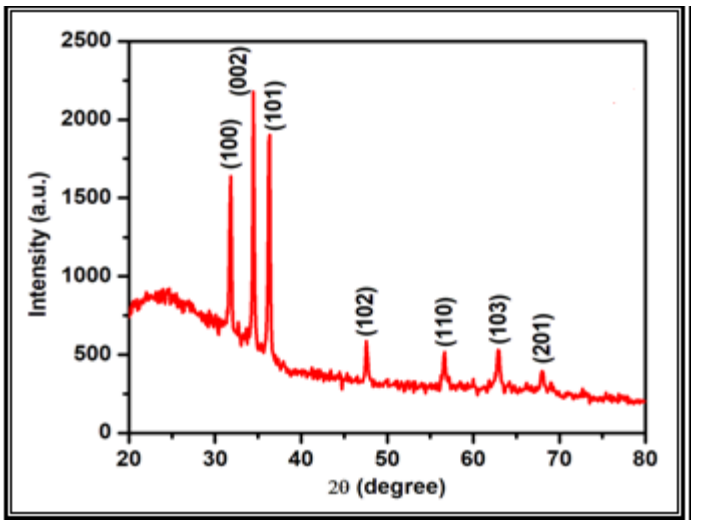

Fig. 1 (a) XRD pattern of ZnO thin film deposited on glass substrate.

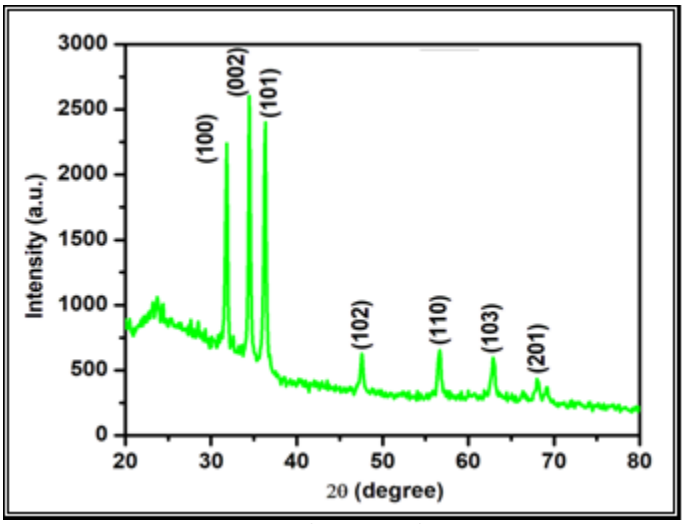

Fig. 1 (b) XRD pattern of ZnO thin film deposited on ITO substrate

XRD pattern of ZnO thin film deposited on ITO substrate was observed at 31.81°, 34.40°, 36.23°, 47.47°, 56.79°, 62.84° and 68.12° corresponding to (100), (002), (101), (102), (110), (103) and (201) planes respectively, which belongs to hexagonal crystal structure with lattice parameters of a = 0.3245 nm and c = 0.5209 nm and coincide the peak with JCPDS data (JCPDS 80-0075, a = 0.3253 nm and c = 0.5209 nm).

The lattice parameters of the film 'a' and 'c' were calculated using the equation.

$$\frac{1}{d^2} = \frac{4}{3}\frac{(h^2 + hk + k^2)}{a^2} + \frac{l^2}{c^2} \quad (1)$$

Where, 'd' is the inter-planar spacing obtained from Bragg's law, and h, k and l are the Miller indices denoting the planes. The average crystallite size has been calculated by using Scherer's formula [14]

$$D = \frac{K\,\lambda}{\beta cos\theta} \quad (2)$$

Where k is constant (0.94), λis the wavelength of X ray radiation (1.54 °A), βis the angular width of the peak at FWHM and θis Bragg's angle.

The determined average crystallite size of ZnO thin film deposited on glass and ITO substrate was found to be 40.1021 nm and 39.2558 nm respectively.

The term dislocation density is nothing but a crystallographic defect in material sciences. It has calculated by using the relation [15].

$$\delta = \frac{1}{D^2} \quad (3)$$

The average dislocation line density of ZnO thin film deposited on glass and ITO substrate was found to be 7.1053 x 10^{14} $(nm)^{-2}$ and 6.9549 x 10^{14} $(nm)^{-2}$ respectively. Table 1 shows a observed and standard 2θ and 'd' values, crystalline size and dislocation density for all planes.

Table 1: Observed and standard 2θ, 'd' values, crystalline size and dislocation density for all planes of ZnO thin film.

Sample	2θ		d values (°A)		Crystalline Size (nm)	Dislocation density x 10^{14}
	observed	Standard	observed	Standard		
ZnO film deposited on glass	31.79	31.72	2.8124	2.8179	43.2926	5.3355
	34.46	34.40	2.6004	2.6049	45.9165	4.7431
	36.29	36.21	2.4733	2.4786	41.3516	5.8481
	47.60	47.49	1.9087	1.9128	32.3013	9.5843
	56.53	56.51	1.6265	1.6269	50.1724	3.9726
	62.90	62.80	1.4763	1.4784	27.5785	13.1480
ZnO film deposited on ITO	31.81	31.72	2.8107	2.8179	43.8534	5.1999
	34.40	34.40	56.51	2.6049	49.4415	4.0909
	36.23	36.21	2.4773	2.4786	44.9686	4.9452
	47.47	47.94	1.9136	1.9128	33.5303	8.8946
	56.79	56.51	1.6197	1.6269	34.7872	8.2634
	62.84	62.80	1.4775	1.4784	35.5683	7.9045
	68.12	67.24	1.3753	1.3601	32.6415	9.3856

3.2 Field Emission scanning electron microscopy (FESEM)

The morphological investigation of the ZnO thin film deposited on glass and ITO substrate was carried out by field emission scanning electron microscopy. Fig. 2 (a) and (b) show the FESEM images of ZnO thin film deposited on glass and ITO substrate with different magnification.

The field emission scanning electron microscopy result revealed that different size of nanorods was observed and nanorods of film deposited on ITO substrate were well distributed as compared to the film deposited on glass substrate. Both films were continuous, dense, crack less, uniform grain distribution homogeneous with covers the entire area.

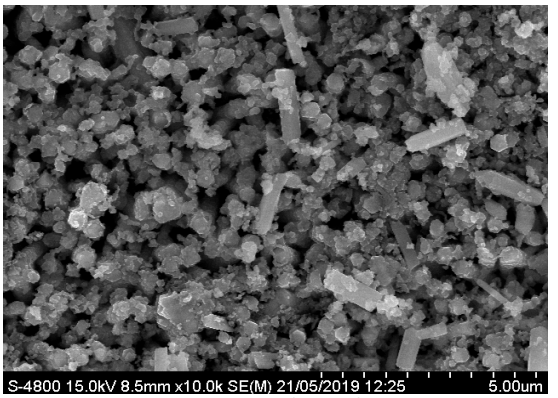

Fig. 2 (a) FESEM micrograph of ZnO film deposited on glass substrate

Fig. 2 (b) FESEM micrograph of ZnO film deposited on ITO substrate.

1.3 Energy dispersive Spectrometer studies (EDS)

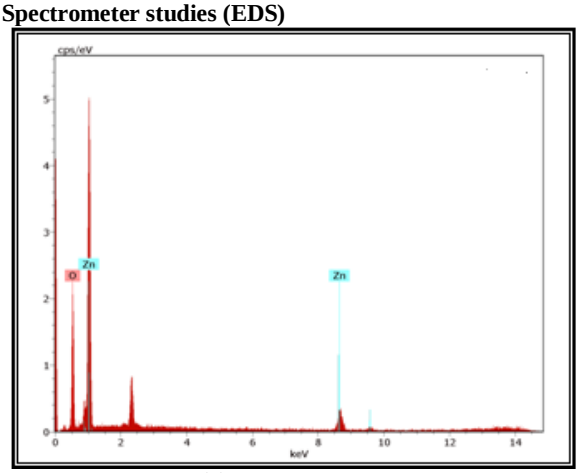

Fig. 3 (a) EDS spectra of film deposited on glass substrate

Fig. 3 (a) EDS spectra of film

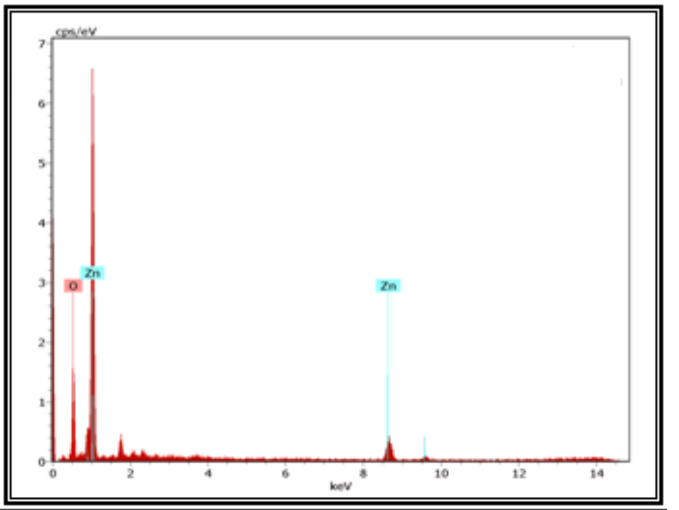

Fig. 3 (b) EDS spectra of film deposited on ITO substrate

The elementary compositional study was carried to obtain the elementary composition of film deposited on glass and ITO substrate using energy dispersive X-ray spectrum (EDS). The elemental analysis showed that the material was only composed of zinc (Zn) and oxygen (O). The atomic percentage of Zn and O atoms was 39.24 and 60.76 for film deposited on glass substrate and 33.05 and 66.95 for film deposited on ITO substrate. Fig. 3 (a) and (b) shows the elementary analysis result. The films were oxygen rich as compare to zinc. Table.2 shows elemental composition of film deposited on glass and ITO substrate.

Table 2: Elemental composition of film deposited on glass and ITO substrate

Sr. No.	Sample	Elements	Atomic (%)
1	ZnO glass	O	60.76
		Zn	39.24
2	ZnO ITO	O	66.95
		Zn	33.05

1.4 Optical properties

Figure 4 (a) and (b) show the variation in absorption spectra of ZnO film deposited on glass and ITO substrate within the wavelength range 200-800 nm. The optical absorption spectra studies revealed that characteristics ZnO band edge absorption at 345 to 351 nm in normalized UV-Vis absorbance. The optical absorption was observed to be slightly increased for film deposited on ITO substrate.

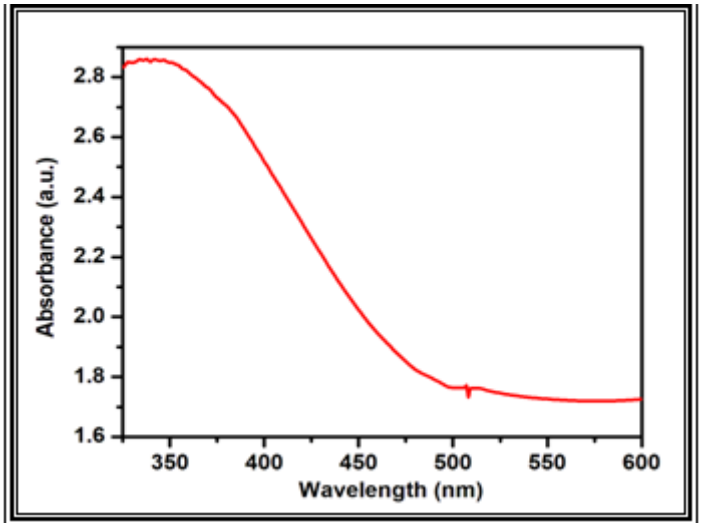

Fig. 4 (a) Absorbance spectra of film deposited on glass substrate

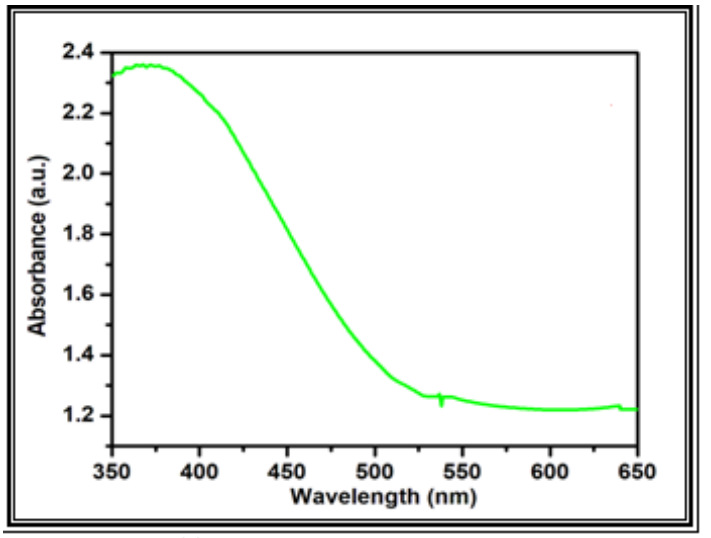

Fig. 4 (b) Absorbance spectra of film deposited on ITO substrate

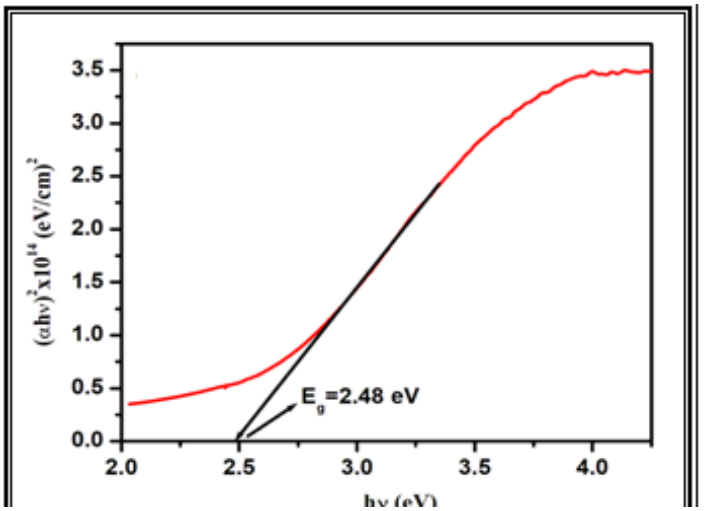

Fig. 5 (a) Plot of $(\alpha h\upsilon)^2$Vs photon energy (hυ) of film deposited on glass substrate

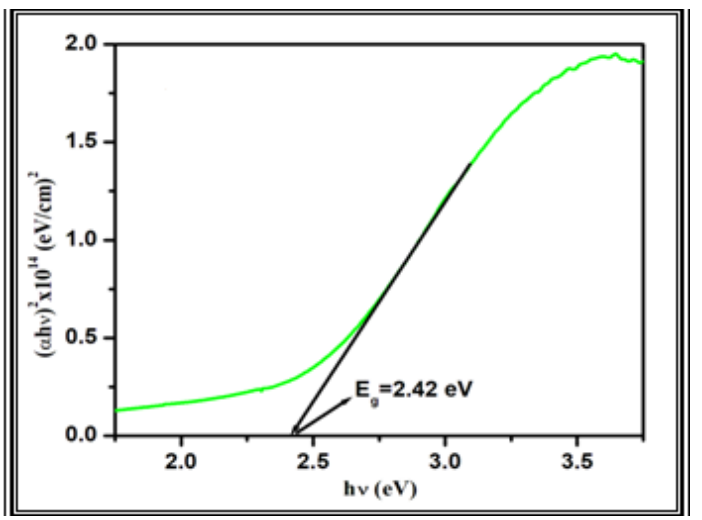

Fig. 5 (b) Plot of $(\alpha h\upsilon)^2$Vs photon energy (hυ) film deposited on ITO substrate

The optical bandgap energy of film deposited on glass and ITO substrate was found out by a graph plotted between $(\alpha h\upsilon)^2$ and photon energy (hυ) is shown in Fig 5 (a) and (b) and has been calculated using the Tauc's relation [16].

$$\alpha h\upsilon = A(h\upsilon - E_g)^n \quad (4)$$

Where α is the absorption coefficient, hυ is the photon energy, E_g the bandgap energy. 'n' is equal to 2 for indirect and ½ for direct band semiconductor respectively [17-18].

The optical bandgap energy of film deposited on glass and ITO substrate was found to 2.48*eV to 2.42* eV respectively. Optical band gap energy slightly decreased for film deposited ITO substrate. Due to the thermal stress effect produced in films optical bandgap of ZnO thin film is less than the reported value [19].

1.5 Electrical resistivity measurement

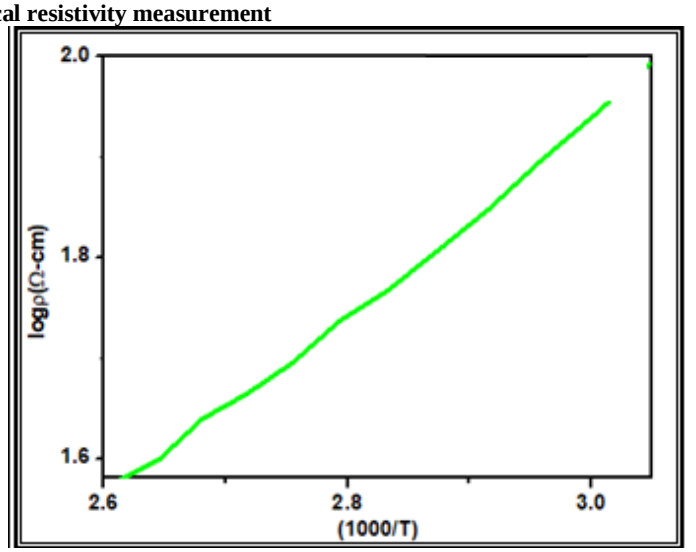

Fig. 6 (a) Plotof Log⟩Vs 1000/T for film deposited on glass substrate

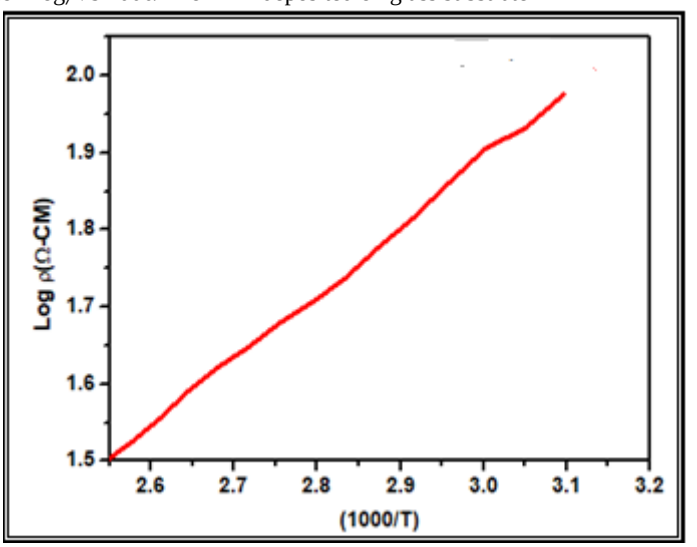

Fig. 6 (b) Plotof Log⟩Vs 1000/T for film deposited on ITO substrate

The electrical properties of ZnO films were studied by using two point probe technique. To study the electrical resistivity for film deposited on glass and ITO substrate, the resistivity measurement was carried out in the temperature range 323 to 423K. The variation of Logρ with 1000/T is shown in Fig.6 (a) and (b).

It is clear that for annealed film, the resistivity decreased and the ultimately conductivity was increased. It was also observed that resistivity decrease with an increase in temperature signifying the semiconductor behavior of zinc oxide thin film [20].

CONCLUSION

1. Low cost, simple and efficient chemical bath deposition method was used to prepare ZnO thin films on glass and ITO substrates.
2. Structural, morphological, optical and electrical characterizations of ZnO thin films were performed.
3. XRD measurement studies indicated that, films deposited on glass and ITO substrates shows polycrystalline structure in the hexagonal phase.
4. Lattice parameters of film deposited on glass substrate was found to be a = 0.3247 nm and c = 0.5201 nm and film deposited on ITO substrate was found to be a = 0.3245 nm and c = 0.5209 nm and coincide with JCPDS data.
5. FESEM studies indicated that, nanorods of ZnO thin films were uniform distributed over the surface for film deposited on ITO substrate than deposited on glass substrate..
6. Optical studies indicated that the bandgap of film deposited on glass and ITO substrate was found to be 2.48 eV and 2.42 eV.

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