

Influence of Co and Fe substitution on optical and structural properties of zinc oxide thin films

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Abstract: Zn_{0.97}TM_{0.03}O (TM = Co, Fe) thin films were deposited onto glass substrates by the sol-gel method and the effects of transition metals substitution on structural and optical properties of ZnO films were investigated. The X-ray diffraction patterns revealed that the films have wurtzite structure. Optical transmittance of the films was recorded in the range of 200 -800 nm wave length and the band gap of the films was determined. The absorption edge of the films showed a small shift depending on the substitution elements. The optical constants of the films were calculated by using pointwise unconstrained minimization algorithm.

Keywords: *Thin film; Sol-gel method; Optical properties; Band gap.*

Introduction

Zinc oxide with band gap energy of about 3.37 eV [1] and high optical transparency in the visible range is a good candidate for application in optoelectronic devices and sensors. Zn_{1-x}TM_xO (TM, transition metal) systems have been investigated to achieve ferromagnetism at or above room temperature [2-4]. These systems due to their coexisting magnetic, semi-conducting and optical properties have the potential for technological applications. It has shown by using Zener model that some diluted magnetic semiconductors (DMS) have Curie temperatures (T_C) above the room temperature, when the hole density is sufficiently high in the compound [5]. It has been suggested that the observed ferromagnetism is related to the interstitial zinc and oxygen vacancies defects in the ZnO [6].

It is found that physical properties of zinc oxide depends on growth method, environmental conditions such as temperature, pressure, doping concentration and also the crystal structure. There

are different chemical and physical methods for growing of ZnO. One of these chemical techniques is the sol-gel method. In this method, environment parameters during the growth of the films affect the properties of the films [7].

In this research, thin films of pure and transition metals (TM) doped ZnO were grown by using of dip sol-gel method. The dopant concentration was kept about 3% and the structural and the optical properties of the films were investigated.

Experimental method

Pure and TM (Fe and Co) doped ZnO thin films were prepared by dip sol-gel method. Zinc acetate dehydrate [Zn(CH₃COO)₂·2H₂O], cobalt acetate dehydrate [Co(CH₃COO)₂·2H₂O], iron chloride [FeCl₂·2H₂O] were used as zinc, cobalt and iron sources and 2-methoxyethanol (DME) [C₃H₈O₂] and mono ethanolamine (MEA) [C₂H₇NO] as solvent and stabilizer respectively. All chemical materials were prepared from Merck Company.

In order to prepare TM doped films, zinc

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acetate and dopant were dissolved in a mixture of DME and MEA solution at room temperature. The molar ratios of MEA to Zn^{2+} and TM/Zn were 1 and 0.03 respectively. The solution was vigorously stirred at 70 °C for 1 h by a magnetic stirrer to yield a clear and homogeneous solution and then aged around 24h at room temperature to obtain the desirable sol. Then the sol was deposited on cleaned glass substrate by dip coating. Undoped ZnO precursor was also prepared in the same way. After coating process, the films were dried at 200 °C for 20 min to evaporate solvent and remove organic residuals. The as-grown films were finally heated at 500 °C for 1h in an open air furnace and then allowed them to cool down gradually to room temperature.

The coated films were prepared to study the optical and structural properties. X-ray diffractometer (Bruker AXS) with CuK_{α} radiation line ($\lambda = 1.5406 \text{ \AA}$) was used to investigate the films crystallite phase and orientation of the films. Diffractometer was adjusted from 30° to 70° with scan step of 0.02°. Surface morphology of the films was studied by using an AFM (model Nanosurf). Optical transmittance was measured by a UV-Vis spectrophotometer (Varian Cary100) at room temperature (RT) which has a 2 nm slit (accuracy 0.1%). The optical constants of the films, refractive index and extinction coefficient, were calculated using point wise unconstrained minimization algorithm and fitting the data to the Cauchy formula [8].

Results and discussion

Structural studies

X-ray diffraction

Figure 1 shows x-ray diffraction patterns of the films annealed at 500 °C which were recorded at room temperature. The diffraction patterns indicate that the $Zn_{0.97}TM_{0.03}O$ films (TM = Co, Fe) and pure ZnO film have wurtzite structure showing prefer (0 0 2) peak. As can be seen from this figure, Co doped sample also shows extra (101) peak. Neither Zn nor Co or Fe characteristic peaks was observed from the diffraction patterns. This result implies that a few percent doping of TM impurities do not change wurtzite structure of ZnO. The grain sizes of the films were estimated from the (002) peak width and Scherrer's formula [9]:

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad (1)$$

where D is the grain size diameter, k is the Scherrer constant, θ is the Bragg angle, λ is the wavelength of x-ray and β is the full width at half maximum (FWHM) of the peak. The results are summarized in Table 1, which are in the range of about 30-33.5 nm. It seems that the grain size likely depends on dopant ionic radius. We calculated the unit cell parameters, a and c, of the films using XRD profiles. The values of unit cell parameters are also shown in Table 1. As can be seen in Table 1, the c parameter of unit cell is directly proportional to dopant ionic radius. This indicates the dopant is substituted in the Zn sites.

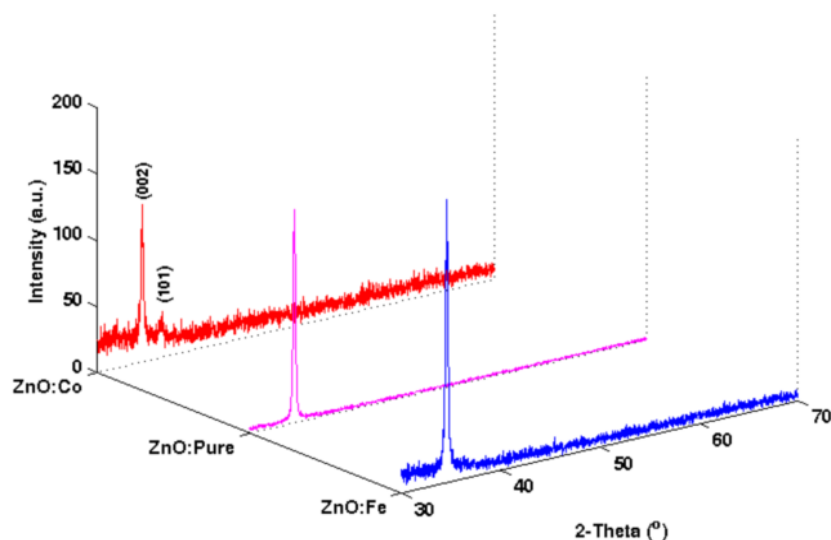


Fig. 1 XRD patterns of the films: ZnO:Fe, ZnO, ZnO:Co.

Table 1. XRD spectrum details of annealed samples in room temperature.

dopant	Ion radius (pm)	Lattice Constant (Å)				Reflection	FWHM (degree)	Roughness Average (nm)	Grain Size (nm)	
		<i>a = b</i>		<i>c</i>						
		Bulk	This work	Bulk	This work					
Fe	Fe ²⁺	63	-	3.249	-	5.207	(002)	0.291	4.25	34.51
Pure	Zn ²⁺	60	3.24	3.249	5.20	5.205	(002)	0.264	2.83	33.25
Co	Co ²⁺	58	-	3.242	-	5.176	(002) (101)	0.262 0.314	2.84	30.17

Surface morphology

Surface topology of thin film is a very important because it can influence physical properties of materials and therefore crystal growth technique, using the various growth methods or changing the primary materials that have been introduced. One of the qualitative parameters of surface is the surface roughness which generally depends on annealing temperature. The annealing temperature also affects the grain size of the films [10]. Figure 2 shows the AFM images of pure and doped ZnO films. All Figures display 3-dimensional topography of the annealed films which were fitted by polynomials.

The roughness average of the film's surface is given in Table 1. As can be seen, the roughness of the pure and Co doped films are nearly the same but larger roughness was observed for Fe doped film. The surface of the Co doped film consists of sharply pointed grain outgrowths. AFM images (2D image) also show that the Co doped film has a smaller grain size.

Optical studies

Transmittance spectrum

Figure 3 (a, b) shows RT transmittance spectra of the films. Figures (a) and (b) are for the as grown films and annealed films at 500 °C, respectively. The transmittance was recorded in the wavelength range 200 to 800 nm with 1nm step. The average transmittance value for the films was about 90% in the optical range. The spectrum of the films without annealing (3-a) shows fluctuation form in visible and infrared regions, whereas the spectrum of the annealed films (3-b) do not show this behavior. Iron doped sample is more transparent than pure and cobalt doped samples. The fluctuation form of the spectrum is referred to

interference of reflections effect on the surfaces of the film [11]. The rough surface will destroy the interference. This result shows increase of the roughness with annealing.

Band gap

Direct band gap of the films can be obtained from equation [12]:

$$(\alpha h\nu)^2 = h\nu - E_g \quad (2)$$

which gives relation between the absorption coefficient α and the photon energy of incident light $h\nu$. Figure 4 indicates the $(\alpha h\nu)^2$ vs. photon energy for the films. The band gaps were determined by extrapolating the linear parts of the corresponding curves with photon energy axis. The extracted band gaps are 3.2718 eV, 3.2778 eV, and 3.2545 eV for undoped ZnO, ZnO:Fe and ZnO:Co films, respectively.

There are many factors which may affect the band gap such as, dopant (Vegard's law), thickness of film, pressure, Moss-Burstein effect, quantum confinement effect due of grain size, magnetic properties of TM impurities, annealing temperature, unwanted potentials of dislocations and etc [13-15].

The band gap of bulk CoO (2.2 eV) is smaller than that of ZnO and in according to Vegard's law [16]:

$$E_g^{ZnO:Co} = (1-x)E_g^{ZnO} + xE_g^{CoO} \quad (3)$$

The band gap of ZnO: Co film should decrease. Reduction of the band gap for the Co-doped ZnO has been reported [17, 18] and explained mainly due to sp-d exchange interactions between the band electrons and the localized d electrons of the Co ions [19, 20].

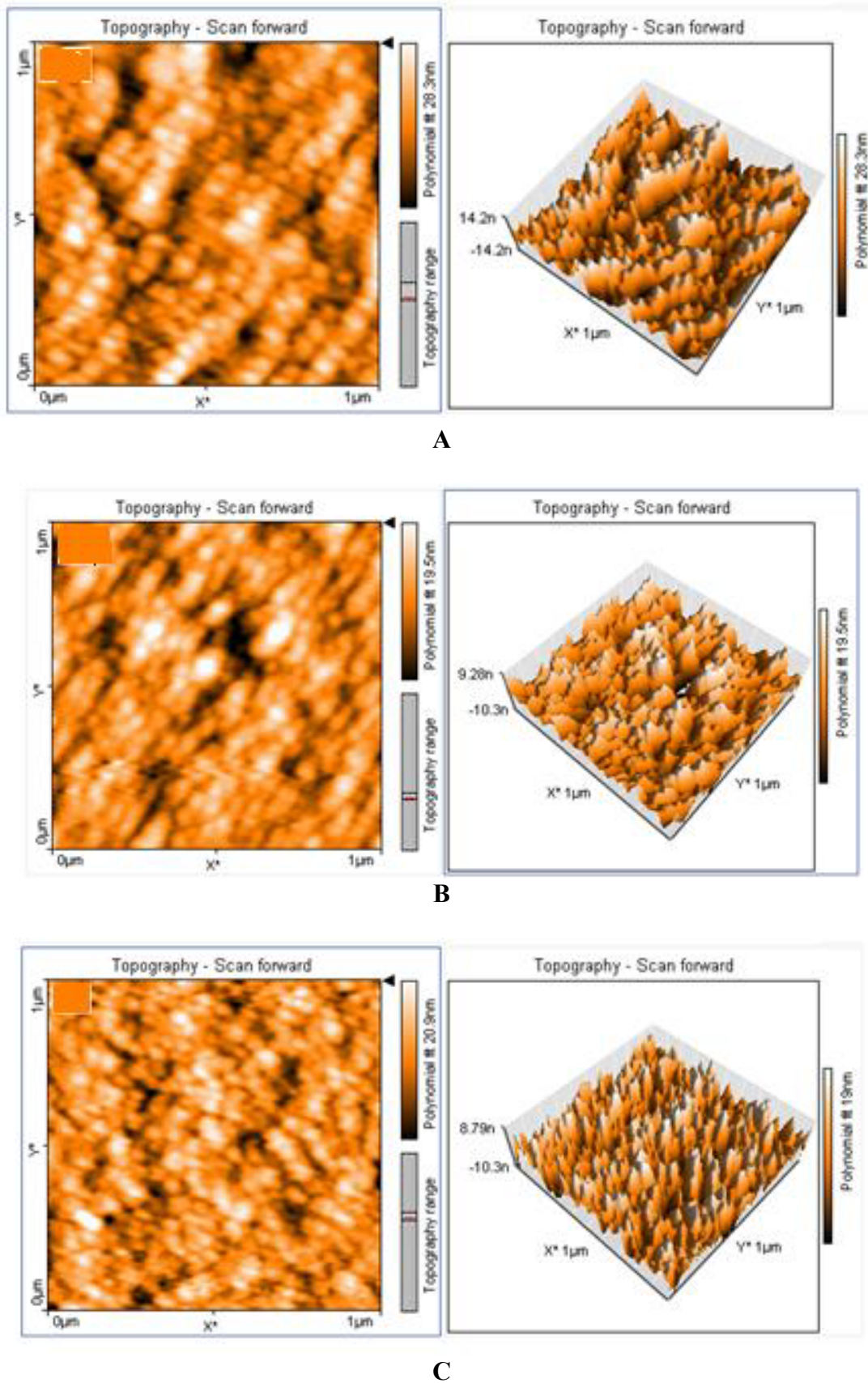
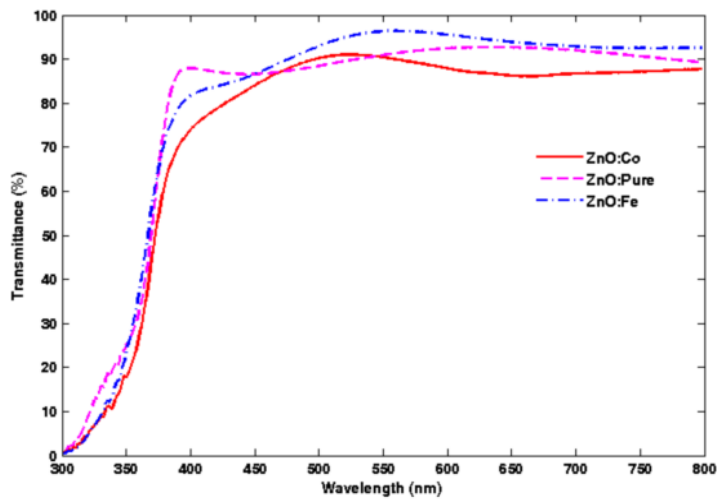
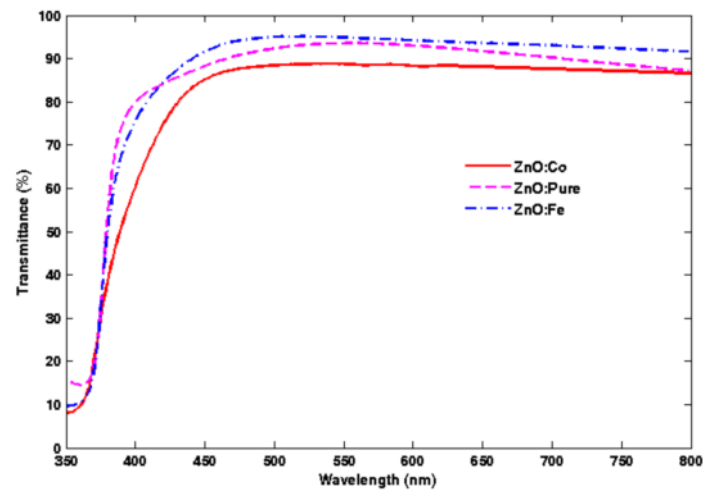


Fig. 2 2D (left) and 3D (right) AFM images of the films: a) ZnO:Fe, b) ZnO, c) ZnO: Co.



A



B

Fig. 3 Transmittance spectra of: a) as grown films b) annealed films.

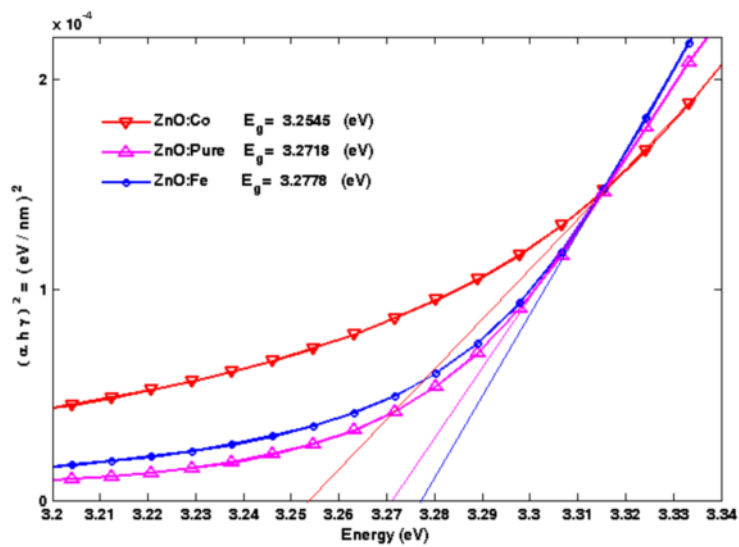


Fig. 4 Plot of $(\alpha h\nu)^2$ vs. photon energy for the annealed films.

Optical constants

The optical constants such as refractive index and extinction coefficient are important parameters for optical materials and their application. These parameters were calculated by using point wise unconstrained minimization algorithm [21]. In this algorithm, by changing the refractive index, n_λ , extinction coefficient k_λ , and thickness d , one can obtain a solution for following equation:

$$T_{theo} = \frac{Ax}{B - Cx + Dx^2} \quad (4)$$

Where A, B, C and D are a function of n , k , λ and T is transmittance. The acceptable solutions in this algorithm are those which make the following relation minimum:

$$\sum |T_{exp}(n, k, d, \lambda) - T_{theo}(n, k, d, \lambda)| \quad (5)$$

Figures 5 and 6 show the dependence of the refractive index and the extinction coefficient of the films on the wavelength. In transparent region of the transmittance spectrum, the refractive indexes of the films don't show remarkable changes and is almost constant and the same. But the extinction coefficients of the films slightly

increases after about 550 nm and also the extinction coefficients value of the films show a little difference which may be due to the different absorption coefficients. Near the absorption edge, around 380 nm, there are noticeable changes due to strong interaction of incident light with carriers of host material.

Penetration depth

Figure 7 shows penetration depth of the films as a function of incident light wavelength. The calculated penetration depths start to increase at the absorption edge until around 500 nm and then decrease. But the upturn points of the penetration depth for three films occur at different energies. Absorption spectra of Co doped ZnO powder showed a visible absorption band around 2.2 eV and attributed to Co^{2+} interatomic d-d transition associated with the crystal field splitting in ZnO [22].

Generally when Zn sites are replaced by TM ions in the sample, this may cause the sample undergo trigonal distortion. The trigonally distorted environment near TM ions may affect the optical properties of the samples [23].

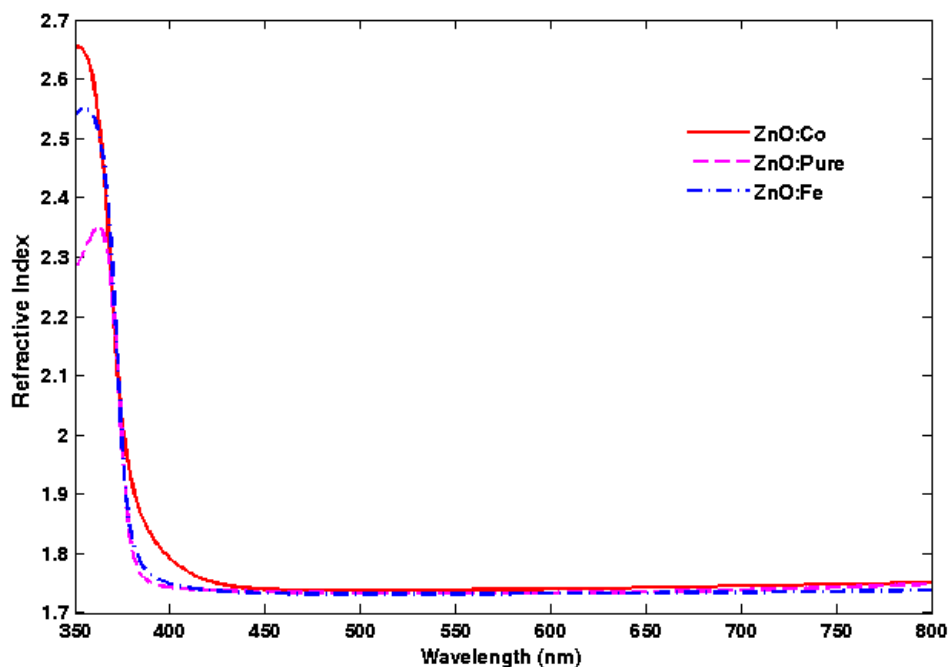


Fig. 5 The dependence of the refractive index of the annealed films on wavelength.

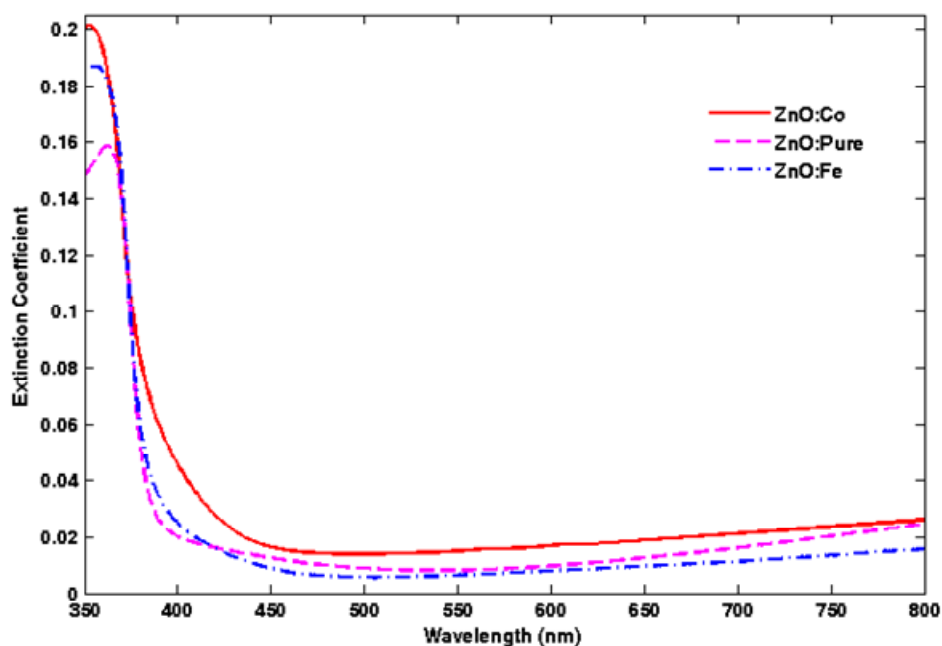


Fig. 6 The extinction coefficient of the annealed films versus wavelength.

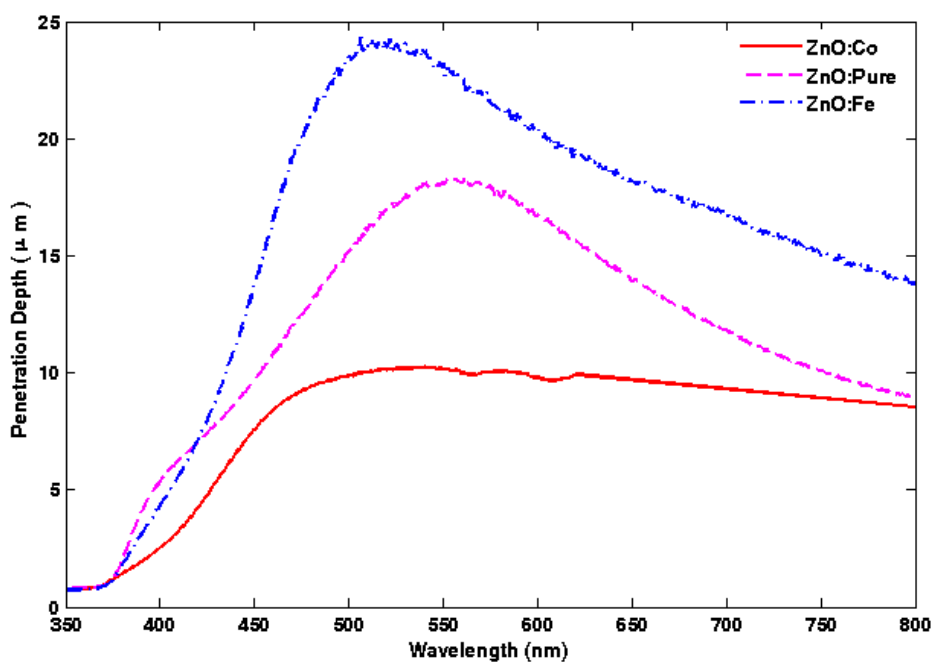


Fig. 7 Penetration depth as a function of wavelength for the annealed films.

Conclusion

In summary, undoped and TM doped ZnO films were grown by sol-gel method. The X-ray diffraction patterns indicated that the $Zn_{0.97}TM_{0.03}O$ films (TM= Co, Fe) and pure ZnO film have

wurtzite structure with prefer (0 0 2) peak. Co doped film also showed extra (101) peak.

The average transmittance value for the films was about 90%. It is observed that the band gap, E_g , of the films vary a little with TM dopant. The

optical constants of the films were calculated with fitting the data by Cauchy formula. The results indicated that the extinction coefficients of the films slightly increase after about 550 nm and also their values show a little difference depends on the dopant.

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