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Study of the structural and optical properties of ZnO and ZnO/Fe₂O₃ thin films grown by chemical bath deposition .

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ABSTRACT:

ZnO and ZnO/Fe₂O₃ composite thin films were prepared by chemical bath deposition technique with thicknesses (150±20) nm. X-ray diffraction analysis showed that pure and composite films polycrystalline in nature with Hexagonal structure and the preferred orientation along (100) plane. The calculated crystallite size of the deposited films are found to be decreases with composite films. The surface morphology of the films was studied by Atomic force microscope, the surface morphology of pure and ZnO composite films are homogeneous distribution. The optical properties of all deposited ZnO and composite films contained study of transmittance and absorbance spectral in the range of wave length (300- 1100)nm, Transmittance increased with composite films. The value of the optical energy gap (E_g) were found decrease with composite films due to the effective electron/holes at the inter faces of ZnO/Fe₂O₃.

KEYWORDS: ZnO/Fe₂O₃ Thin films, composite, Structural and optical properties, (CBD).

1. INTRODUCTION

Nanocrystalline materials, among them ZnO semiconductor nanocrystals doped with 3d metal ions (Fe, Ni, Co, Mn), received considerable attention as potential components of future nanotechnology. Thin films of ZnO have been studied as the active material in the development of thin film transistors due to their n-type semiconductor characteristic and excellent thermal stability, and can be well-oriented crystalline in various substrates. (S.A. Wolf, et, al, 2001), (Masuda, S, et, al, 2003). Most prominent crystalline structure of ZnO is wurtzite type, although, it also exists in the cubic zinc blende and Hexagonal structures. In wurtzite type, each Zn ion is surrounded by a tetragonal coordination. This give rise to polar symmetry along the hexagonal axis, which is responsible for a number of properties of ZnO (Ramamoorthy, K, et, al, 2004). Thin films have been widely used in transparent electrodes, surface acoustic wave devices, field effect transistors and display devices. ZnO is a useful, economical and environmental semiconductor material because of its typical properties such as a wide direct band gap (3.3 eV) (Y. Yan, et, al., 2009), (Pankove, J. I. (1971).

2. Experimental part

The glass substrates of 75x25x1 mm dimensions were washed with Laboratory detergent and rinsed with distilled water in abundance water and acetone for several times in ultrasonically cleaned and finally dried in air. Thin film of ZnO and composite ZnO/Fe₂O₃ nanostructure were grown glass substrate by using chemical bath deposition (CBD) technique. ZnO films were prepared using aqueous solutions of zinc (II) chloride (ZnCl₂) 1M in de-ionized water to the volume of 100ml under magnetic stirring about 5 minutes and 0.1 M Iron chloride solution was prepared in 100 ml of di-ionized water using magnetic stirrer for 5 minute and NaOH 3M in de-ionized water to the volume of 50 ml under magnetic stirring about 5 minutes after solution (NaOH) was added 10ml drop wise into the mixed solution. The measured pH value at the step varied between 9.8 and 11. Prior to the deposition, the beaker containing the deposition solution was placed in the water bath at 80 °C for about 5 minutes to stabilize the temperature of the solution, then the beaker was kept in the water bath. At the end of the deposition time (1 hour), the slides were taken out, rinsed

with distilled water and allowed to dry with warm air. Samples were Characterized using with X-ray diffraction type (SHIMADZU Japan XRD 6000) to identify the crystal structure of the prepared films, The surface morphology was analyzed by Atomic Force Microscope (AFM) device type (SPM AA3000 /Angstrom Advanced Inc.), Optical spectrums of the films were recorded by UV-Visible Shimadzu 1800 spectra photometer

3. Results and Discussion

3.1 Structural properties

The crystallite size (D) was calculated using Scherrer's formula [11].

$$D = \frac{k\lambda}{B\cos\theta} \quad (1)$$

Where K: is Scherer constant and that is equal to $[2(\ln 2/\pi)^{1/2} = 0.94]$ λ : wavelength, and B: full width at half In radian.

The absorption coefficient(α) determine according to the following equation [12].

$$\alpha = 2.303 \frac{A}{t} \quad (2)$$

Where t is film thickness , A is the film absorption .

The optical band gap E_g^{opt} was calculated By Tauc relation[12] .

$\alpha h\nu = B(h\nu - E_g^{opt})^r$ (3) Where $h\nu$ is photon energy, B constant depends on the nature of the material , and r is the value depends on the nature of the transition .

The Study of ZnO and composite ZnO/Fe₂O₃ thin films were analyzed for their structural properties by recording X-ray diffraction pattern , Fig.(1) shows the XRD pattern of ZnO films which was deposited on glass substrates at bath temperature 353 K for deposition time 1 hr. The peaks from the diffraction patterns were found to be characteristic to ZnO and composite ZnO/Fe₂O₃ thin films compared with standard ICD card No. 00-036-1451. All films exhibit peaks related to polycrystalline Hexagonal structure with preferential orientation of (100) plane

(LinhuaXu,et,al,2010),(Sreeja,et,al,2010) . As shown in table1.

Fig1: XRD pattern of deposited ZnO and composite ZnO/Fe₂O₃ .

Figure (2a,b). presents AFM two dimensions (6.19 μm $\times$ 6.19 μm) (2D , 3D) images From this images by Atomic force microscope , the surface morphology of pure and ZnO composite films are non-homogeneous distribution (Das, et al.,2007).

Fig. 2. AFM images (2D , 3D) of a: ZnO b: ZnO/Fe₂O₃.

Tab1.1. XRD result of deposited ZnO and composite ZnO/Fe₂O₃ .

Material	ZnO	ZnO/Fe ₂ O ₃
2 θ (deg)	31.6	32.2
d(Å) Observed	2.82	2.77
d(Å) Standard	2.81	2.81
FWHM (deg)	0.1998	0.23610
(hkl)	(100)	(100)
Average crystalline Size (nm)	43.18	36.59

4.2 Optical Properties

The optical transmittance spectra of ZnO and composite ZnO/Fe₂O₃ thin films within the wavelengths of the range from (300 – 1100) nm. Fig3a. Shows the transmittance as a function of the wavelength of ZnO and composite ZnO/Fe₂O₃ thin films. where it can be observed an increase in transmittance by increasing the wavelength. It was also observed that the transmittance increasing by composite ZnO/Fe₂O₃ thin films . Fig3b. Shows that the absorbance as a function of the wavelength of ZnO and composite ZnO/Fe₂O₃ films, where observe the absorption values decrease by increasing the wavelength, it can be seen decreasing with composite ,This spectrum reveals that ZnO/Fe₂O₃ film have low absorbance Because Iron effect on crystalline composition of material (Xu, L,et,al,2010) ,(Sreeja,et,al,2010). .

Fig3. a. optical transmittance curves of ZnO and composite ZnO/Fe₂O₃

Fig3. b. the optical absorption curves of ZnO and composite ZnO/Fe₂O₃ .

Fig.4 the absorption coefficient as a function of the energy photon ($h\nu$) , it can be seen that the films have a high absorption coefficient ($\alpha > 10^4 \text{ cm}^{-1}$) which indicates direct electronic transitions.

Fig4. absorption coefficient of ZnO and composite ZnO/Fe2O3 thin films.

The optical energy gap has obtained from intercept of the extrapolated linear part of the curve with the photon energy axis ($h\nu$) at $(\alpha h\nu)^2 = 0$. The linear nature of the plots at the absorption edge confirmed that all deposited films are a semiconductor with direct band gap. These results showed that E_g^{opt} is (3 , 2.8) eV of ZnO and composite ZnO/Fe2O3 respectively, and composite have low ZnO/Fe2O3. Because the conduction band of ZnO lies above Fe2O3, which reduce the energy gap (Choudhury, N, et, al, 2009), (Pierson, H. O., 1999).

Fig5. The optical energy gap of ZnO and composite ZnO/Fe2O3 thin films

5. Conclusions

Chemical bath deposition method is an easy and inexpensive to prepare ZnO thin films. XRD studies of

ZnO and composite ZnO/Fe2O3 films indicated the formation of nanocrystalline with polycrystalline hexagonal phase, and the average crystallite size are equal to (43.18 , 36.59) nm respectively. thin films by Atomic force microscope , the surface morphology of pure and ZnO composite films are homogeneous distribution. The high optical transmittance in wavelength region ($T > 500$ nm) , its advantageous features of ZnO thin films that works as filters, and antireflection coating to improve solar cell efficiency, It was also observed that the transmittance increasing by composite ZnO/Fe2O3 thin films. The optical gap The films have allowed direct transition and the optical energy gap values (3 , 2.8) eV of ZnO and composite ZnO/Fe2O3 respectively and composite have low ZnO/Fe2O3. Because the conduction band (CB) of ZnO lies above Fe2O3 which reduce the energy gap (Pierson, H. O., 1999).

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