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Effect of difference concentrations of Al on the optical properties of AZO thin films

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Abstract: *Effect of difference concentrations on the optical properties of AZO thin films, prepared on glass slides by Sol-gel method .The optical characteristics of the prepared thin films have been investigated by UV/Vis spectrophotometer in the wavelength range (200 – 800) nm .The films have a direct allow electronic transition with optical energy (Eg) values decreased from 3.29eV for AZO 1% thin films to 3.28eV for the AZO 2% films and to 3.04eV for the AZO 3% films. The maximum value of the refractive index (n) for all thin films are given about 2.13. Also the extinction coefficient (K) and the real and imaginary dielectric constants (€1 & €2). The results indicate the films have good characteristics for optoelectronic applications.*
Keywords: *ZnO, thin films, optical properties*

I. Introduction

Transparent conducting oxides (TCOs) are electrical conductive materials with a comparably low absorption of light. (TCO) films have emerged as excellent candidates due to interest in their promising applications in next-generation electrode. A wide variety of transparent conductors in terms of new materials are becoming available that could serve as an alternative to ITO [1]. ITO is one of the best transparent conductors, but indium is quite expensive [2]. The electrodes fabricated utilizing TCO films in optoelectronic devices have excellent physical properties of high visible transmittance, low resistivity, high infrared reflectance, and large absorbance [3]. Because ZnO materials are large-band-gap semiconductors with peculiar physical properties of high chemical stabilities and large exciton binding energies, they are of current interest due to their potential applications in optoelectronic devices, such as photo detectors, solar cells, light-emitting diodes, and laser diodes. Low-resistivity ZnO thin films may be realized by using several dopants, such as Al, Ga, and In of the group III [4].

Aluminum doped zinc oxide (AZO) coatings exhibit high transparency and low resistivity and these materials are suitable for fabricating transparent electrodes in solar cells, gas sensors and ultrasonic oscillators. They are also found in applications such as surface acoustic devices, optical waveguides and micro-machined actuators. They are an alternative material to tin oxide and indium tin oxide, which has been most, used up to date [4].

For the most used (ITO) as a transparent conducting oxide which has transmittance (≥90%), low specific resistance (≤10-3 Ω/cm) in the visible rays area, so it is used as the transparent electrode of the solar cell, display fields widely. But the raw materials of ITO are expensive, and it has weak point of the degradation phenomenon and toxicity when it is exposed in the hydrogen plasma [4-2]. The Al of doped ZnO(AZO) thin film is cheap and controlling of specific resistance is easy, and the wavelength of the visible rays shows the high transmittance, so a lot of studies on the transparent conducting oxide are being conducted [5].

In several studies, it was shown that the optical and electrical properties of AZO thin films could be obviously improved by optimized deposition conditions and doping. Additionally, the opto-electrical properties of AZO thin films could be modified by thermal treatment in a reducing atmosphere. The indium doped ZnO films grown at deposition temperature of 400 °C and 450 °C showed an improved crystallinity (exturization along the c-axis) which resulted in a strong decrease of the resistivity. Ohyama reported that the use of 2-methoxyethanol and monoethanolamine, solvents with high boiling point, resulted in transparent ZnO films with strongly preferred orientation and that better electrical and optical properties had been obtained in 0.5 at.% aluminum doped ZnO thin films heated in reducing atmosphere. Nunes found that when the doping concentrations of Al, In and Ga were 1, 1 and 2 at.%, respectively, electrical and optical properties of doped ZnO were superior [2].

Various techniques such as molecular beam epitaxy (MBE) [6], pulse laser deposition (PLD) [7], magnetron sputtering [8], chemical vapor deposition (CVD) [9], atomic layer deposition [10], electron beam evaporation [11], hydrothermal method [12], and sol-gel process [13] have been applied to ZnO thin film preparation. The sol-gel method has distinct potential advantages over these other techniques owing to its lower

crystallization temperature, low cost, simple deposition procedure, easier compositional control, ability to tune the microstructure via sol-gel chemistry, and large surface area coating capability.

In this work, undopedZnO and AZO thin films were prepared by the sol-gel method with different Al concentrations. The optical properties of the AZO thin films were investigated. In particular, optical parameters such as the optical band gap, absorption coefficient, refractive index and extinction coefficient, real and imaginary dielectric constant were comprehensively studied in order to investigate the effects of Al doping on the optical properties of AZO thin films.

II. Experimental

The precursors used in the synthesis ZnO and AZO seed layers by sol-gel process are Zinc acetate dehydrate Zn(CH3COOH)2.2H2O and Aluminum nitrate nonahydrate Al(NO3)3.9H2O. The need for surfactant is fulfilled by the use of 2-methoxyethanol (ME) CH3OCH2CH2OH. The stock solution for the samples was prepared using Zinc acetate 0.1M, dissolved in 300 ml of ethanol in the glass beaker. Then the solution was stirred for 60 min at 80°C until we get milky solution. Drops from 2-methoxyethanol (ME) was added to the solution as stabilizer to get a transparent solution. We get then the Zinc oxide solution. The solution was divided into six mount of 50ml in six beakers.

In order to add Al doping into ZnO, another solution was prepared by dissolving Aluminum nitrate nonahydrate 0.1M in 50 ml of ethanol. By calculating the ratio of doping, we added Al doping to the ZnO solution with kept the total volume at 50 ml with stirring at same temperature before. Three of the solutions were doped with Al for the ratios of 1%, 2% and 3%. The four mounts of solutions have been leaved in lab's temperature about 24 hours, then we filter it, and we obtained the Sol ready to be used to prepare the film by spinner (spin coating). The films were prepared in microscope glass slide. At glass slices were cleaned with ethanol. Then, they were washed with deionized water and acetone. The coating of films on glass slice was performed at room temperature, with suitable speed rate for 30 s. The deposited film is preheated at 150 oC for 5 min to evaporate the water and then at 450 oC for 30 min to enhance the crystalline of the prepared films. After cleaning the other side of substrate with hydrochloric acid, they were ready for characterization.

The thicknesses of the AZO thin films were about 359.3 nm for 0 at.%, 267.8 nm for 1 at.%, 249 nm for 2 at.%, and 223.4 nm for 3 at.%. The optical transmittance and reflectance of the AZO thin films were measured as a function of wavelength by UV-visible spectroscopy

III. Results and discussion

The absorption coefficient (α) of the prepared ZnO thin films also of the difference concentration were found from the following relation [14]

$\alpha = 2.303\ A/t$ (1)

Where (A) is the absorbance and (t) is the film thickness.

Fig. (1) shows the plot of (α) with wavelength (λ), which obtained that the value of $\alpha > 6x10^6\ cm^{-1}$ for all films in the UV and visible region , this means that the transition must corresponding to a direct electronic transition [15] , and the properties of this state are important , since they are responsible for electrical conduction. Also, fig (1) shows that the value of (α) for the AZO 3% concentration films are greater than that ZnO films. The increase in absorbance of AZO 3% concentration thin films, may be due to the increase in grain size and decrease in the number of defects as explained by Al [16]

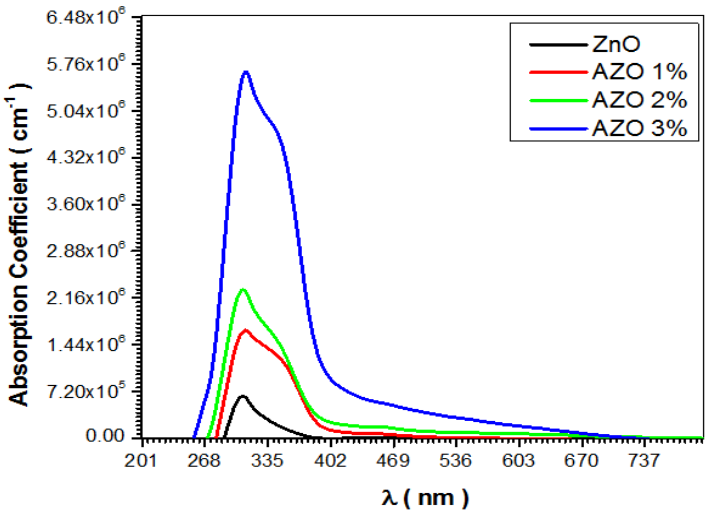

Fig. (1). the variation of absorption coefficient (α) with (λ) for thin films

The optical energy gap (Eg) has been calculated by the relation [17]
$(\alpha h\upsilon)^2 = C(h\upsilon - Eg)$ (2)
Where (C) is constant. By plotting $(\alpha h\upsilon)^2$vs photon energy (hυ) as shown in fig.(2).And by extrapolating the straight thinportion of the curve to intercept the energy axis , the value of the energy gap has been calculated [17] The value of(Eg) obtained was 3.69eV, which is approach the value of 3.69eVreportedelsewhere [18] .The value of (Eg) was decreased from3.29eV at 1% to 3.28eV at AZO 2% concentration and to 3.04eV at AZO 3% concentration. The decreasing of (Eg) may be related to decrease in grain boundaries and their density due to the heating effect of the polycrystalline thin films. It was observed that the different structures of the films confirmed the reason for the band gap shifts. The behavior of (Eg) was agreement with researcher [16, 19].

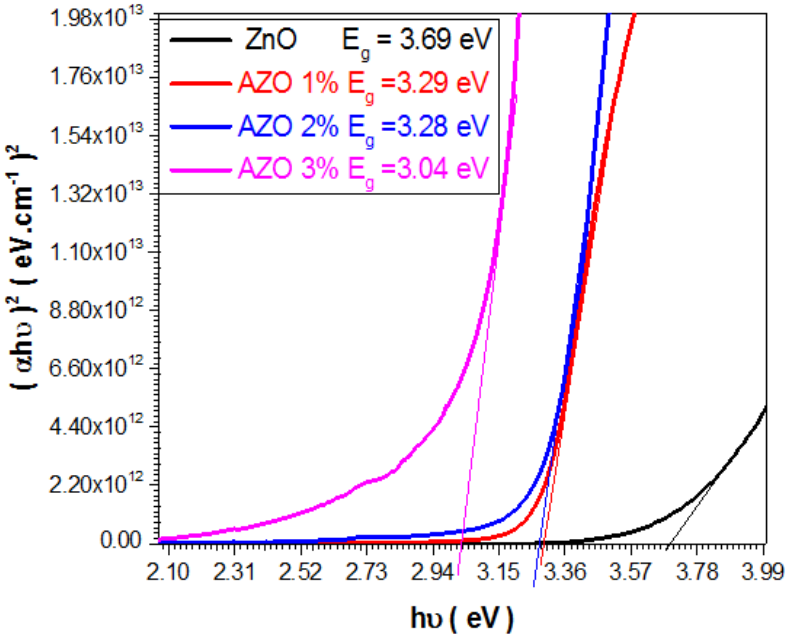

Fig. (2). The optical energy gap (Eg)value of thin films

Extinction coefficient (K) was calculated using the related [14].

$$k = \frac{\alpha\lambda}{4\pi} \quad (3)$$

It is observed that the spectrum shape of(K) as the same shape of (α).Fig.(3)obtained the value of (K) at the UV region was depend on the film treatment method , where the value of (K) at 312.1nm for AZO 3% concentration film is 0.14 while for AZO 2% concentration film at the same wavelengthequal0.06 and for AZO 3% concentration film equalto0.04 at the same wavelength ,this difference in (K) value become smaller at UV region .

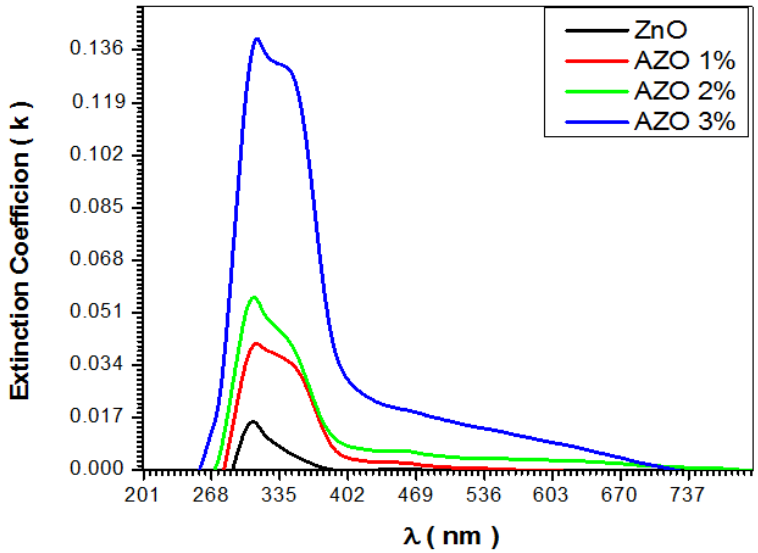

Fig. (3). The variation of extinction coefficient (K) with wavelength (λ) for thin films

The refractive index (n) is the relative between speeds of light in vacuum to its speed in material which does not absorb this light. The value of n was calculated from the equation [14]:

$$n = \frac{1+R}{1-R} + \left(\frac{4R}{(1-R)^2} + k^2\right)^{\frac{1}{2}} \quad (4)$$

Where (R) is the reflectivity. The variation of (n) vs (λ) is shown in fig (4).Which shows that the maximum value of(n) is 2.13 for all films at the same wavelength which is agreement with ref. [18]. Also we can show that the value of (n) begin to increase in the region of spectrum while (K) in its region became constant .Also (n) value decrease with AZO 1% concentration film, this means that the film become more transparent inthe361.97 nm(UV)region.

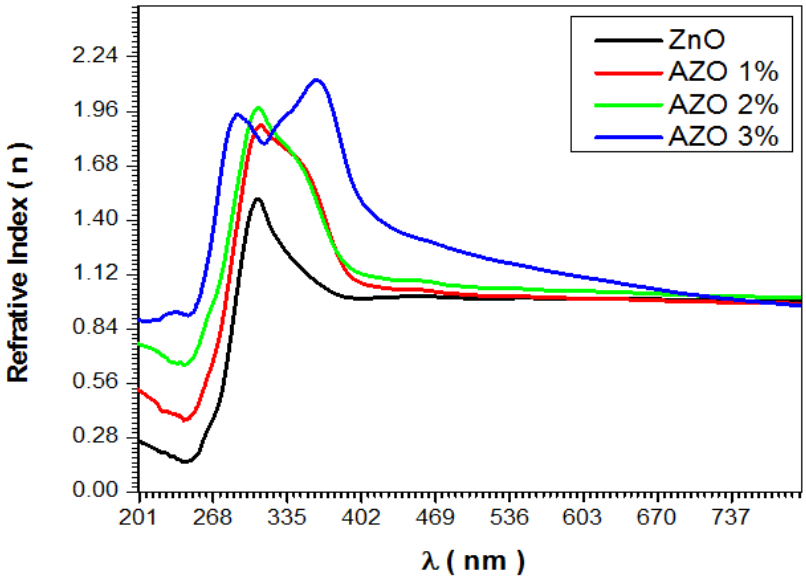

Fig.(4). The variation of refractive index(n) with wavelength (λ) for thin films

Fig.(5) shows the variation of the real dielectric constant (Є1) with wavelength of ZnO thin films, which calculated from the relation [14]

$Є1 = n^2 – K^2$(5)

Where the real the dielectric (Є1) is the normal dielectric constant.

From fig (5)the variation of (Є1) is follow the refractive index, where increased in the region that λ >361.97 nm, where the absorption of the film for these wavelength is small, but the polarization was increase. The maximum value of (Є1)equal to 4.51 for all films at wavelengthnear361.97 nm. The effect of AZO 3% concentration of thin films decreased (Є1) in the region below451.83 nm wavelength.

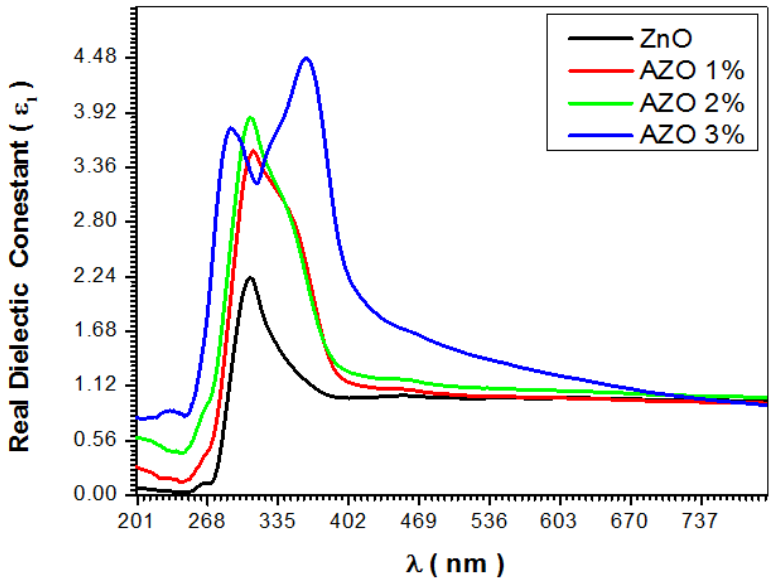

Fig. (5). The variation of (Є1) with wavelength (λ) for thin films

The imaginary dielectric constant (€2)vs(λ) was shown in fig. (6) This value calculated from the relation [14]:
€2= 2nK (6)
(€2) represent the absorption associated with free carriers [20] .As shown in fig (6) the shape of (€2) is the same as (€1), this means that the refractive index was dominated in these behavior. The maximum values of (€2)are different according to the treatment operation, so the maximum value of (€1)for AZO 3% concentration thin film equal to 0.521at345.39nm, while €2= 0.221 at λ = 308.75nm for AZO 2% concentration thin film, and €2 = 0.149at λ = 312.07 nm for AZO 3% concentration thin films, these behavior may be related to the different absorption mechanism for free carriers.

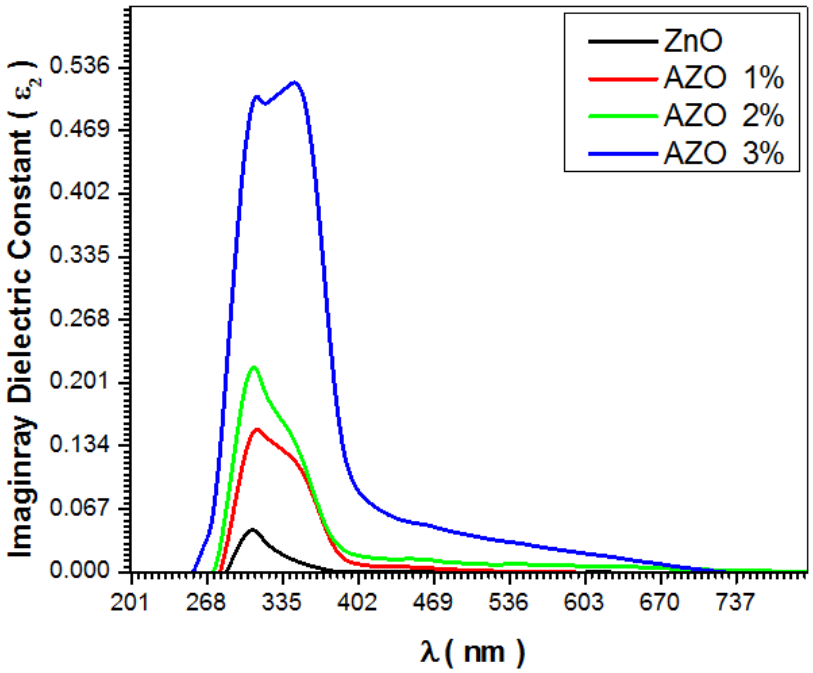

Fig. (6). the variation of (€**2**) with wavelength (λ) for thin films

IV. Conclusions

ZnO thin films deposited by Sol-gel method shows band gap3.69eV which under AZO 1% concentration was found to be 3.29eV and3.28eV at AZO 2% concentration. Under these treatment the film shows a shift of 0.41eV for AZO 2% concentration and3.04eV for AZO 3% concentration in its optical spectra .Such dependence has been attributed to the structure of the film. The extinction coefficient value was increased in the UV region with treatment. The films give refractive index value equal to2.13 in the 345.39 (UV-region).Hence, these treatment for thin film give a best optical properties to be used for optoelectronic Applications.

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