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Physics Properties Comparison Between Undoped ZnO and AZO, IZO Doped Thin Films Prepared By Spray Pyrolysis

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Abstract: In this study, the comparison of physics properties between undoped ZnO and Aluminium AZO and Indium IZO doped zinc oxide thin films was done. The most physics properties are structural as X-rays diffraction patterns, optical as reflectance and transmittance spectra and electrical as resistivity measurement at room temperature. Namely the zinc oxide with wurtzite structure is deposited by spray pyrolysis on corning glass substrates at kept temperature. Photoconductivity was significantly changed by doping.

Key words: ZnO thin films, AZO, IZO, transmittance, electrical resistivity, photoconductivity

INTRODUCTION

Zinc oxide has been widely studied as a direct wide band gap (3.2 eV) with an hexagonal wurtzite structure. It is an inexpensive n-type semiconductor (Chopra *et al*., 1983). ZnO presents a piezoelectric properties. It finds application in surface acoustic wave devices (Sundaram and Khan, 1997). Because of its high optical transparency and electrical conductivity, it have been used as window layers, anti-reflecting coating in solar cells (Gal *et al*., 2000). ZnO is used as gas sensors (Golego *et al*., 2000). These have been deposited by many techniques as sputtering (Jayaraj *et al*., 2002), ultrasonic spray pyrolysis (Ma *et al*., 1996), chemical vapor deposition (Sato *et al*., 1994), sol-gel (Bao *et al*., 1998), IBAD (Zhang *et al*., 1997), laser ablation (Narasimhan *et al*., 1997), spray pyrolysis (Studenikin *et al*., 1998).

The addition of impurities as aluminium or Indium, induces a high electrical conductivities and a good transparency in the visible region.

Zinc atoms are substituted by trivalents atoms (X^{3+}, Where X = Al, In). It has been pointed out that extrinsic donors due to doping atoms are more stable than the intrinsic donors due to the native defects.

Spray pyrolysis technique has been used to elaborate IZO and AZO films (Changhyun, 1996; Joseph *et al*., 2005; Kuo *et al*., 2006).

The last technique is very useful, more reproducible, without toxicity. More ever incorporation of dopants is easier in this technique. Recently, p-type ZnO have been made and widely studied by Pearton *et al*. (2005). In this study, we have investigated the effect of doping on zinc oxide by keeping the deposition parameters constants.

MATERIALS AND METHODS

The experimental techniques synthesis was done in Electron Microscope Laboratory Sciences and Technology University (2002) and the characterizations were realized in the center for Energy Research-UNAM Mexico (2002).

Our ZnO samples were thin films. They were deposited by spray pyrolysis method. The precursor compound used was zinc acetate dehydrated Zn $(C_2H_3O_2)_2$. $2H_2O$, while aluminium nitrate ($Al(NO_3)_3$. $9H_2O$) and indium trichloride $InCl_3$ were used as doping source. Both, precursor and doping compound were dissolved in the methanol. The zinc acetate concentration was 0.2 M and the doping ratio Al/Zn, In/Zn were fixed at 2% in the solution. Corning glasses slides were used as substrates. The deposition temperature was kept at 285°C and the deposition time was 220 sec.

The film thickness was measured by Scanning electron microscopy. The structural properties was studied using X-ray diffraction. Optical transmission and reflection were obtained in the range wavelength 300-2500 nm with a double beam spectrophotometer. Film resistance has been determined by a four points technique.

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In order to obtain the photo current response of the samples, two metals contacts were deposited onto the samples using silver print. After that, the samples were kept in dark up to 10 h after the experiment A voltage of 10V was applied in the contact during 20 sec under dark conditions, 20 sec under 100 m watts cm^{-2} illumination by Xenon power and 20 sec under dark again.

The current across the samples was recorded automatically.

RESULTS AND DISCUSSION

All the studies done in this work were carried out in samples with thickness of 0.55 μm.

Structural properties: The corresponding X-Rays diffraction for undoped and doped films, in the range of scanning angle $30° < 2\theta < 70°$ are shown in Fig. 1 (Al 2%, In 2%).

The average crystallite grain size is calculated using Scherrer Formula (Cullity, 1978).

$$d = \frac{0.94\lambda}{B\cos\theta} \quad (1)$$

where λ is the X-ray wavelength equal to 1.54 Å, θ is Bragg diffraction angle and B(radians) is the full-width at half maximum.

All films are polycristallines with hexagonal wurtzite type.

Figure 1 shows that undoped films consist of irregularity oriented grains according to (001) (002) and (101) directions with a weak peak (002). This results has been obtained by different authors for sprayed zinc oxide as (Studenikin *et al.*, 1998; Paraguay *et al.*, 1999; Krunks and Mellikov, 1995). The average grain size is estimated to be 26 nm in the direction (002).

The ZnO: Al thin films (AZO) grows preferentially with the (002) plane, also it was observed peaks at (102) and (103) as has been reported by Jin *et al.* (1999), Ma and Lee (2000). Aluminium doping reduced the cristallite size to 22 nm. Many researchers have reported that the cristallite grain size decrease with the increase doping level An increase in doping concentration deteriorates the cristallinity of the films. This is can be due to the difference in ion size between zinc and the dopant (r_{zn}^{2+} = 0.074 nm, r_{Al}^{3+} = 0.054 nm), dislocations, segregation of dopants in the grain boundaries (Jin *et al.*, 1988; Islam *et al.*, 1993; Kuo *et al.*, 2006; Lee and Park, 2004).

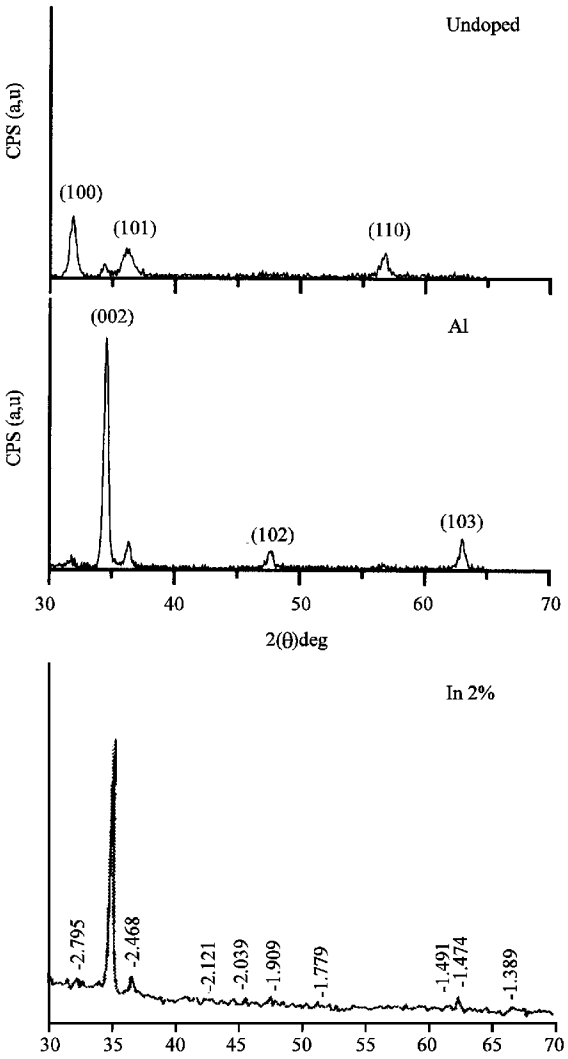

Fig. 1: XRD patterns of ZnO thin films deposited at 285°C

The ZnO: In thin films (IZO) exhibited a strong peak; this corresponds to the (002) orientation The grains grows in this direction. Indium doping enhances the crystallite grain sizes to 46 nm. So, the doping by indium improve cristallinity. The same tendency was observed by Changhyun *et al.* (1996), Joseph *et al.*(2005) and Kotlyarchuk *et al.* (2005).

Optical properties: Optical properties were measured in the 250-2500 nm range. Spectral transmittance as doping type prepared at 285°C are plotted in Fig. 2. The doping improves the transmittance. IZO films show high transmittance (95%) than AZO (85%).

Films were transparent in the visible region. It's a direct consequence of their being a wide band gap semiconductors (Chopra *et al.*, 1983).

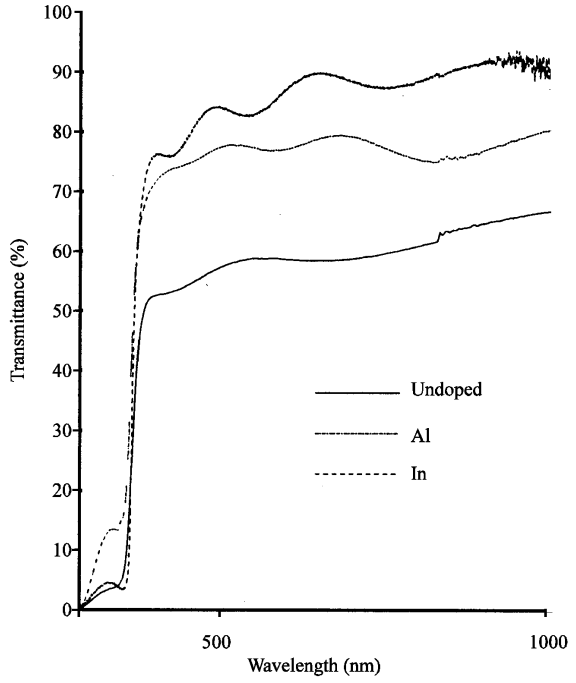

Fig. 2: Optical transmittance spectra of ZnO films IZO, AZO and undoped

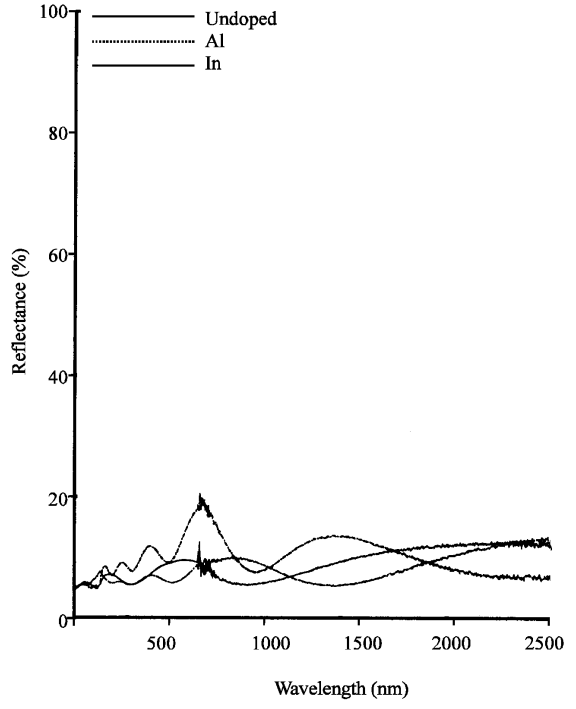

Fig. 3: Reflectance of ZnO, AZO, IZO films

The films exhibit a minimum in the reflectance spectra (Fig. 3). Such minimum is expected to take place near the plasma frequency.

This is due to the existence of plasma resonance in this films, The plasma frequency ω_p and the reflectance minima ω_{min} are given by the relation (Narasimhan *et al.*, 1997).

$$\omega_p^2 = \omega_{min}^2 \frac{\varepsilon_r}{\varepsilon_r - 1} \quad (2)$$

where ε_r is the relative dielectric constant and ω_p found values were 1.54, 2.43 and 1.13E15 s^{-1} forundoped, AZO and IZO films, respectively.

The absorption coefficient α is deduced from the spectral transmittance using the relation. Joseph *et al.* (2005):

$$\alpha = \frac{\ln(\frac{1}{T})}{t} \quad (3)$$

where T is the transmittance and t is the films thickness.

The optical gap were obtained by plotting $(\alpha h\nu)^2$ versus $h\nu$, where $h\nu$ is the photon energy. We used the method described by Major *et al.* (1986) Eg has 3.27, 3.35 and 3.32 eV for undoped, AZO and IZO films. These values were also reported by Islam *et al.* (1993), Studenikin *et al.* (1998) and Kuo *et al.* (2006), Joseph *et al.* (2005).

We found that the optical gap is slightly small than the bulk value. The effect of interaction electron-electron, defects and impurities leads to a reduction in the optical gap bulk values.

The direct band gap, as determined from Fig. 4 depend on the electron density and the so called band effective mass.

$$E_g = E_{g0} + \frac{h^2 n^{2/3}}{8\pi^{2/3} m^*_{eff}} \quad (3)$$

where Eg_0 is the fundamental direct band gap, n and m^*_{eff} are the density and the effective mass of electrons, respectively. The second term is called Burstein-Moss, the latter contributes in the gap enlargement ΔE known as Moss-Burstein energy.

This expression suggests that optical gap is broadened as the free charge carriers concentrations enhances.

The doping effect was associated with the excess of zinc atom acting as a donor. The point defects can be interstitials or oxygen vacancies. The free electron increases in proportion with the doping atoms increasing

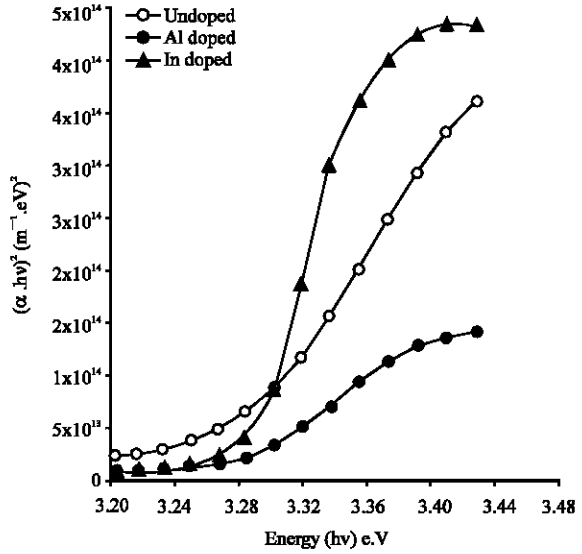

Fig. 4: Plots of absorption against photon energy for ZnO films

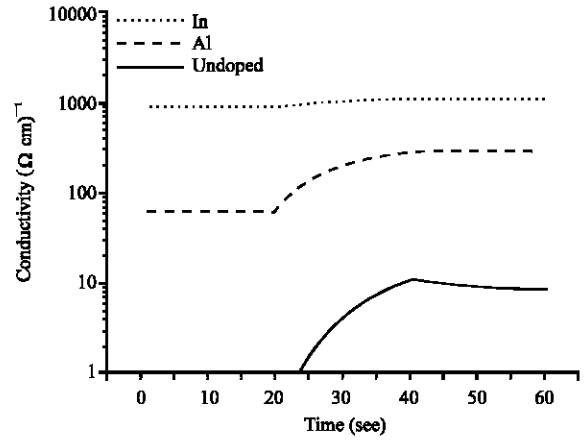

Fig. 5: Photoconductivity versus time of ZnO films (effect of doping)

in the film network. The impurities are singly ionized and the associated electrons occupy the bottom of conduction band as a free electron gas (Jin *et al*., 1988).

Electrical properties: The resistivity of undoped and doped films and the concentrations are regrouped in Table 1. It was found that the resistivity is strongly depended on the doping.

The undoped films resistivity is about 17 Ω-cm whereas the AZO and IZO films resistivity are about 1.8E-2Ω-cm and 6.7 E-3Ω-cm, respectively. When a small amounts of third group element (Al or In) was incorporated into ZnO films, this element take interstitial position and acts as donors. Also, a larger grains size d in IZO films induced a decrease in resistivity. The

Table 1: Resistivity and concentration values for undoped ZnO, AZO and IZO

Physics properties	Resistivity (Ω cm)	Concentration (cm^{-3})
Undoped	17	7.7E17
AZO	1.8E-2	2.24E19
IZO	6.7E-3	4.43E20

Table 2: Comparison of experimental parameters among previous and present study

Experimental parameters	Subs Temp (°C)	Time deposition	Dopant
Present parameters	285	220 sec	Nitrate d`Alumium $InCl_3$
Joseph *et al.* (2005)	400		$InCl_3$
Lee and Park (2004)	500	45 min	$AlCl_3$
Kotlyarchuk *et al.* (2005)	480		$InCl_3$
Ma and Lee (2000)	240		$AlCl_3$
Jin *et al.* (1999)	450	30 min	$AlCl_3$

mobility is proportional to d and this caused a large number of free electrons. The increase in carrier concentration is due to a small amount of oxygen vacancies and a large amount of desorption of oxygen chemisorbed at grains boundaries. Indium doping effect on the resistivity is more pronounced than aluminium.

Transient photoconductivity: A plot of the photoconductance as function of time is shown in Fig. 5.

We could see that the photoconductivity arise with doping. The effect of illumination is to neutralize negative charge in the surface states, Electron-hole pairs created in the bulk of crystallites mainly recombine via radiative of Shockly-Read Hall mechanisms. Holes can be captured by deep traps at the grain boundary resulting in increase in number of free electrons which are unable to recombine.

This can be explained by the removed oxygen from the grain boundary and this caused a decrease in the density of acceptors states at the grain boundary, resulting in the capture of a small numbers of bulk electrons by these state acceptor.

For undoped films, the decay observed in the photoconductance is due to adsorption of oxygen. Absorbed oxygen captured an electron from the conduction band and became chemically absorbed, accompanied by photoconductivity decrease (Melnick, 1957; Eger *et al*., 1975).

We showed a very slow decay photoconductivity in doped films. This is attributed to a slow electron-hole recombination. The same conclusion is reported by Studenikin *et al*. (2000) and Zhang *et al*. (2001).

The conductivity was not assigned by the exposition of the thin films to illumination in the AZO and IZO cases as shown in Changhyun *et al*. (1996).

The originality of our research consists in the experimental parameters as substrate temperature T_s and deposition time t_d and kind of dopant compared to those made by authors and details were given in Table 2.

CONCLUSIONS

Undoped ZnO, Al and In doped ZnO thin films deposited by spray pyrolysis technique at a temperature 285°C were investigated to be used as transparent conductors. The impact of doping on the structural, optical and electrical properties were studied. Also, it was studied the effect of illumination on the electric properties.

XRD indicates that the cristallinity enhance with the indium doping but the average crystallite grain size decrease with the aluminium doping. This could be attributed to the formation of stresses by the difference in ion size between zinc and the dopant. Doping improve the transmittance films So these films are highly transparent. The magnitude of the optical band gap obtained is ins agreement of many reports. It varies from 3.27 to 3.35 eV. The doping improve the resistivity by reducing the height of grain boundaries and caused a deficiency in oxygen. This caused an important number of free electrons.

Under illumination, the photoconductivity falls up with doping. U.V radiation generates electron-hole pairs. The photoconductivity was due to capture of non equilibrium holes by surface state. This increase free carriers density The processus adsorption-desorption had an important effect on the slow photoconductivity.

It can conclude that the indium doping improve the cristtalinity of the films in the direction (002), the conductivity, and the transmittance is about (95%).

The Al doping seems to improve the photoconductivity by reducing traps density. This is not affected by the illumination. So, the stability of the electrical properties is enhanced.

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