Effect of Halogen Doping on Optical Properties for ZnO Thin Film Prepared by Thermal Oxidation

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ABSTRACT: Undoped and halogen-doped zinc oxide thin films are prepared by the thermal oxidation process. Zinc acetate dihydrate, ethanol, and Diethanolamine are used as precursor, solvent, and stabilizer, respectively. In the case of ZnO:Hal. dopant Ammonium chloride NH_4Cl 99%, Benzene Bromide $\text{C}_6\text{H}_5\text{Br}$, or Benzene Iodide $\text{C}_6\text{H}_5\text{I}$ for making dopant ZnO thin film with Cl, Br, I respectively is added to the precursor solution with an atomic percentage equal to 2-10.% hal. The transparent solution sprayed onto glass substrates, and are transformed into ZnO upon annealing at 500°C . XRD spectra of ZnO thin films, and optical properties of them as a function of halogen content have been investigated using U.V spectroscopy (transmittance , refractive index, extinction coefficient and energy band gap) for undoped and halogen-doped zinc oxide thin films.

1. INTRODUCTION

ZnO thin film is one of the II-VI compound semiconductors and is composed of hexagonal wurtzite crystal structure. ZnO thin film presents investigating optical, and electrical properties which meet extent applications in the fields of electronics, optoelectronics and sensors. ZnO thin film is applied to the transparent conductive film and the solar cell window because of the high optical transmittance in the visible region [1-5]. ZnO can be a *n*-type and a *p*-type semiconductor determined by the dopant nature [6,7]. *n*-Type doping of ZnO is relatively easy compared to *p*-type doping [7] and reproducible *p*-type conductivity, However, *p*-type doping in ZnO may be possible by substituting either group-I elements (Li, Na, K, *etc.*) for Zn-atoms or group-V elements (N, P, As, Sb, *etc.*) for O-atoms [6-9], For *n*-type [6,7,9-12], doping with group-III elements (B, Al, Ga, In), as substitutional elements for Zn, has been attempted by many groups, resulting in high-quality, optically transparent, and highly conductive ZnO films as this substitution of divalent Zn^{2+} by a trivalent ion generates an excessive free electron. Especially, Al-doped ZnO (AZO) thin films have attracted a considerable amount of interest due to their good electrical conductivity with reasonably low optical loss [13].

On the other hand, *n*-type semiconductors may also be synthesized by substituting O-atoms by group-VII elements (F, Cl, Br, I) [7]. The ZnO thin film is prepared using various methods such as spray pyrolysis, sputtering, sol-gel spin coating, pulsed laser deposition (PLD), chemical vapor deposition (CVD) [14–17]. In spite of few studies regarding to Thermal Oxidation method, the Oxidation method has some merits, such as the easy control of chemical components, and fabrication of thin film at a low cost to investigate structure and optical properties of ZnO thin films. Optical properties of thin films are very important for the designing of solar cells and optoelectronic devices. In particular, the information about optical constants such as refractive index(*n*), the extinction coefficient (*k*) and energy band gap (E_g) play a vital role in the designing of optoelectronic devices. They are extensively used for characterization of composition of material over a wide range of wavelength in optic devices [18].

2. EXPERIMENTAL

2.1. Experimental procedure [19-21]

To synthesize the ZnO solution, 10.95 gr of zinc acetate dehydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$) from Prolabo lot (*687G) $M=219.5$ gr/mol was first dissolved in an ethanol solvent (ethanol absolut puriss.p.a.) from Sigma-aldrich lot (82499) in a 100 ml flask and was stirred for 15 min at room temperature to yield a milky solution then 2.5 ml of diethanolamine (DEA) from Merck was dropped carefully to the solution as a stabilizer, the complex solution was stirred for other 15 minutes until get a transparent, homogenous, and stable sol. We used ethanol, cause of a low boiling point and non-toxicity solvent.

Un-doped ZnO thin films were coated onto pre-cleaned glass substrates Soda-lime $5 \times 2 \text{ cm}^2$ by spray the solution on it, each coated film was heated at 500°C for 50 minutes then annealing to room temperature.

For dopant ZnO thin film we add a fixed amount of dopant Ammonium chloride Extra pure NH_4Cl 99% Labo Chemie India, Benzene Bromide $\text{C}_6\text{H}_5\text{Br}$ from Merck 99% $M=157.02$ gr/mol, Benzene Iodide $\text{C}_6\text{H}_5\text{I}$ from BDH 98% $M=204.01$ gr/mol for making dopant ZnO thin film for Cl, Br, I respectively.

Doped ZnO thin were coated onto pre-cleaned glass substrates Soda-lime $5 \times 2 \text{ cm}^2$ by spray the solution on it, each coated film was heated at 500°C for 50 minutes then annealing to room temperature.

A flow chart .1 summarize the experimental procedure for pure and dopant ZnO thin film flowchart .1 The experimental procedure for pure and dopant ZnO thin film

3. RESULTS AND DISCUSSION :

3.1 Crystalline characterization by XRD measurements

Philips analytical X-Ray Diffractometer type PW1840 at ALBAATH University was used with tube anode copper Cu at wavelength $\lambda = 1.54 \text{ \AA}$ from $2\theta = 30-70^\circ$, figure 1 displays the XRD spectrum of ZnO pure thin films. Three lines (100) at $2\theta = 31.77^\circ$, (002) at $2\theta = 34.4^\circ$, and (101) at $2\theta = 36.25^\circ$ are pointed, they will be considered for structural characterization of ZnO.

Figure 1: ZnO Pure thin film XRD Spectrum.[21,22]

We measured the XRD spectra for ZnO: Halogen with different Hal. ratio from 2% to 10 % and found the following results represented in figure 2.

Figure 2: XRD Spectrums for ZnO: Hal.

A significant evolution of the resolutions of ZnO (100), (002) and (101) characteristic lines is obtained. The increase of Cl concentration in the starting material for the ZnO preparing process, leads to an amorphous stage of the films at 10 % ratio, while we get an amorphous stage directly when we use Br or I as a dopant agent, and we think it refers to the atom size cause the atom size of Cl is near the same of oxygen while the atom size for Br or I is bigger and leads to get more defects in the crystal orientation of ZnO

3.2 Optical properties

3.2.1. Transmittance:

3.2.1.1. Transmittance for each halogen depends on dopant ratios:

U.V Spectroscopy has Model V-570 and Serial No. C02 96774 at ALBAATH University was used to measure the transmittance of these thin films by using these parameters:

Band width 2.0 nm, Measurement range 1100 - 400 nm, Data pitch 2nm, Scanning speed 400 nm/min, Figure 3 displays the measured transmittance of the ZnO pure and ZnO:Hal. films in the range 400nm to 1100 nm for 2-10% ratios of Halogen dopants

Figure 3: ZnO and ZnO:Hal. for 2-10% ratios of Halogen dopants thin films transmittance spectroscopy
a) ZnO: Cl for 2-10% ratios, b) ZnO: Br for 2-10% ratios, c) ZnO: I for 2-10% ratios

3.2.1.2. Transmittance for halogens at fixed dopant ratios:

Figure 4 displays the measured transmittance of the ZnO pure and ZnO:Hal. films in the range 400 nm to 1100 nm at fixed dopant ratios from 2% - 10 %

Figure 4: ZnO and ZnO:Hal. for 2-10% ratios of Halogen dopants thin films transmittance spectroscopy
a) ZnO:Hal for 2%, b) ZnO: Hal for 4%, c) ZnO: Hal for 6% d) ZnO: Hal for 8% e) ZnO: Hal for 10%

3.2.2. Refractive indices:

3.2.2.1. Refractive index for each halogen depends on dopant ratios:

Figure 5 displays the calculated Refractive indices of the ZnO pure and ZnO:Hal. films in the range 400nm to 1100 nm for 2-10% ratios of Halogen dopants

Figure 5: ZnO and ZnO:Hal. for 2-10% ratios of Halogen dopants calculated Refractive index
a) ZnO: Cl for 2-10% ratios, b) ZnO: Br for 2-10% ratios, c) ZnO: I for 2-10% ratios

3.2.2.2. Refractive index for halogens at fixed dopant ratios:

Figure 6 displays the calculated refractive indices of the ZnO pure and ZnO:Hal. films in the range 400 nm to 1100 nm at fixed dopant ratios from 2% - 10 %

Figure 6: ZnO and ZnO:Hal. for 2-10% ratios of Halogen dopants thin films transmittance spectroscopy
 a) ZnO:Hal for 2%, b) ZnO: Hal for 4%, c) ZnO: Hal for 6% d) ZnO: Hal for 8% e) ZnO: Hal for 10%

3.2.3. The extinction coefficient (k):

3.2.3.1. The extinction coefficient for each halogen depends on dopant ratios:

Figure 5 displays the calculated The extinction coefficient of the ZnO pure and ZnO:Hal. films in the range 400nm to 1100 nm for 2-10% ratios of Halogen dopants

Figure 5: ZnO and ZnO:Hal. for 2-10% ratios of Halogen dopants calculated the extinction coefficient
a) ZnO: Cl for 2-10% ratios, b) ZnO: Br for 2-10% ratios, c) ZnO: I for 2-10% ratios

3.2.3.2. The extinction coefficient for halogens at fixed dopant ratios:

Figure 6 displays the calculated the extinction coefficient of the ZnO pure and ZnO:Hal. films in the range 400 nm to 1100 nm at fixed dopant ratios from 2% - 10 %

Figure 6: The extinction coefficient of ZnO and ZnO:Hal. for 2-10% ratios of Halogen dopants
a) ZnO:Hal for 2%, b) ZnO: Hal for 4%, c) ZnO: Hal for 6% d) ZnO: Hal for 8% e) ZnO: Hal for 10%

3.2.4. Energy band gap

The energy band gap could be obtained from spectroscopy measurements, and we found the following results:

3.2.4.1. Energy band gap for each halogen depends on dopant ratios:

Figure 7 displays the energy band gap of the ZnO pure and ZnO:Hal. films in the range 400nm to 1100 nm for 2-10% ratios of Halogen dopants

Figure 7: The energy band gap of ZnO and ZnO:Hal. for 2-10% ratios of Halogen dopants
a) ZnO: Cl for 2-10% ratios, b) ZnO: Br for 2-10% ratios, c) ZnO: I for 2-10% ratios

3.2.4.2. Energy band gap for halogens at fixed dopant ratios:

Figure 8 displays the energy band gap of the ZnO pure and ZnO:Hal. films in the range 400 nm to 1100 nm at fixed dopant ratios from 2% - 10 % and we can summarize the whole results in table .1

Figure 8: The energy band gap of ZnO and ZnO:Hal. for 2-10% ratios of Halogen dopants
a) ZnO:Hal for 2%, b) ZnO: Hal for 4%, c) ZnO: Hal for 6% d) ZnO: Hal for 8% e) ZnO: Hal for 10%

Table.1 Summarize the whole results which we get from our research as follows:

Sample	Trans. Range %	Medium of trans.%	Refractive index range	Medium of refractive index	extinction coefficient range	Medium of extinction coefficient	Energy band gap e.V
ZnO Pure	60.0-95.1	87.0	1.56-2.36	1.84	0.012-0.028	0.017	3.20
ZnO:Cl2%	66.0-99.7	91.7	1.35-2.30	1.68	0.005-0.025	0.012	3.19
ZnO:Cl4%	58.0-98.5	88.8	1.44-2.46	1.79	0.007-0.033	0.015	3.15
ZnO:Cl6%	49.3-97.1	85.9	1.51-2.61	1.90	0.010-0.045	0.020	3.10
ZnO:Cl8%	34.7-86.2	70.3	2.01-2.57	2.35	0.030-0.067	0.040	2.90
ZnO:Cl10%	20.1-75.3	54.6	2.39-1.93	2.50	0.060-0.102	0.076	2.30
ZnO:Br2%	46.2-91.7	80.4	1.79-2.63	2.06	0.025-0.049	0.026	3.00
ZnO:Br4%	41.3-90.1	77.5	1.83-2.64	2.15	0.023-0.053	0.050	2.90
ZnO:Br6%	49.5-91.6	79.6	1.75-2.63	2.09	0.020-0.059	0.030	2.90
ZnO:Br8%	42.9-88.9	76.8	1.80-2.64	2.16	0.022-0.054	0.030	2.90
ZnO:Br10%	34.5-85.7	73.9	1.91-2.56	2.23	0.027-0.067	0.036	2.70
ZnO :I 2%	59.5-92.7	83.8	1.64-2.46	1.95	0.015-0.033	0.020	3.10
ZnO :I 4%	54.6-90.6	80.7	1.72-2.53	2.04	0.018-0.037	0.025	3.06
ZnO :I 6%	49.3-93.3	82.6	1.63-2.62	2.00	0.015-0.045	0.024	3.00
ZnO :I 8%	45.8-95.2	83.5	1.58-2.64	1.98	0.013-0.049	0.023	2.88
ZnO :I 10%	31.4-85.9	71.7	1.93-2.49	2.29	0.029-0.074	0.041	2.60

From table .1 we can see that transmittance for ZnO:Cl 2% is the best and near to ZnO pure , then the transmittance for the other goes lower with more dopant ratios, and it refers to the atom size of the dopant, but we notice the transmittance in total of ZnO:I is better than ZnO:Br and we think it refers to Iodide in based solution convert to I^- and IO_3^- colorless which lead to more transparent thin films and get better transmittance, and for refractive index we get 1.84 , and 2.3 e.V for energy band gap that match with literature, and we get increasing with refractive index and decreasing of energy band gap with increasing of dopant ratios.

4. CONCLUSION

Undoped and halogen-doped zinc oxide thin films are prepared by the thermal oxidation process. Zinc acetate dehydrate, ethanol, and Diethanolamine are used as precursor, solvent, and stabilizer, respectively. In the case of ZnO:Hal. dopant Ammonium chloride NH_4Cl 99%, Benzene Bromide C_6H_5Br , or Benzene Iodide C_6H_5I for making dopant ZnO thin film with Cl, Br, I respectively is added to the precursor solution with an atomic percentage equal to 2-10.% hal. The transparent solution sprayed onto glass substrates, and are transformed into ZnO upon annealing at 500°C. XRD spectra of ZnO films show three lines (100) at $2\theta = 31.77^\circ$, (002) at $2\theta = 34.4^\circ$, (101) at $2\theta = 36.25^\circ$ which pointed to structural characterization of ZnO and which disappeared directly when Br, I was a dopant and which will decrease with increasing with Cl dopant ratio, and optical properties of the thin films as a function of halogen content have been investigated using U.V spectroscopy (transmittance , refractive index, extinction coefficient and energy band gap) for undoped and halogen-doped zinc oxide thin films were studied and found that transmittance for pure ZnO was 60-95.1% and go better for ZnO:Cl 2% (66-99.7%) then it goes lower with increasing of Cl dopant ratio, while for ZnO :Br was 46.2-91.7% and for ZnO :I was 59.5-92.7%, refractive index for pure ZnO was 1.84 and for ZnO:Cl 2% was 1.68, while ZnO :Br and ZnO :I have refractive index about 2.06 , 1.95 respectively, extinction coefficient for pure ZnO was 0.012-0.028 and for ZnO:Cl 2% was 0.0005-0.025, while ZnO :Br and ZnO :I have extinction coefficient about 0.019-0.025,0.015-0.033 respectively, and for energy band gap for pure ZnO was 3.20 e.V and for ZnO:Cl 3.19 and goes lower with increasing of dopant ratio till 2.3 e.V for ZnO :Cl 10% , while ZnO :Br and ZnO :I 10 % have energy band gap 2.7, 2.6 e.V respectively.

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