Journal of Electron Devices, Vol. 16, 2012, pp. 1347-1355

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Journal of Electron Devices
www.jeldev.org

THE MORPHOLOGY AND I-V CHARACTERISTICS OF $Zn_{1-X}Mg_XO$ THIN FILMS DEPOSITED BY SPRAY PYROLYSIS TECHNIQUE

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Received 29-11-2012, online 6-11-2012

ABSTRACT

Mg doped ZnO thin films were deposited on a glass substrate by spray pyrolysis technique at a substrate temperature equal to (400℃) under ambient atmosphere. The energy-dispersive X-ray analysis (EDX) spectra of the $Zn_{1-X}Mg_XO$ thin films reveals that all the films contain the elements (Zn, Mg, O) as expected, indicating formation of the $Zn_{1-X}Mg_XO$ films with high purity. From the (SEM) images the grain size values of the $Zn_{1-X}Mg_XO$ thin films deposited by (SP) technique are found to be in the ranges of (59-83)nm, (35-59)nm, (47-71)nm, (47-59)nm, (35-47)nm corresponding to the Mg-concentrations (x = 0, 0.1, 0.2, 0.3, 0.4) respectively. The I-V characteristics of $Zn_{1-X}Mg_XO/n-Si$ heterojunction for dark and illuminated conditions have been investigated.

Keywords: thin film, $Zn_{1-X}Mg_XO$, spray pyrolysis

I. INTRODUCTION

ZnO with bandgap ($E_g \sim 3.4eV$) has been investigated intensively due to its potential applications for laser diode (LD) and light emitting diode (LED) at ultraviolet or even blue light spectra. More interestingly, its large exciton binding energy ($\sim 60meV$) makes the efficient excitonic emission at room temperature possible. For the development of ZnO film based optoelectronic devices, the realization of p-type conductivity ZnO thin film is considered to be a critical issue and has been investigated by various doping techniques[1,2].

Although ZnO is a hexagonal wurtzite-type structure ($a = 3.253Å, c = 5.213Å$) and MgO is a cubic sodium chloride (NaCl) type structure ($a = 4.213Å$), the similarity in ionic radii between $Zn^{2+}(0.74Å)$ and $Mg^{2+}(0.71Å)$ allows significant Zn/Mg replacement in either structure, while the lattice parameters are kept almost constant. Since the modulation of the bandgap with similar lattice constant is essential for construction of the heterojunction or superlattice to obtain high-performance (LD) and (LED) devices, hexagonal $Zn_{1-X}Mg_XO$ alloy film was found to be a very suitable barrier layer for ZnO/ $Zn_{1-X}Mg_XO$ superlattices [3] and multi-quantum wells [4].

Heterojunctions of TCO/Si have been reported to have good photovoltaic characteristics [5]. Since ZnO is a wide bandgap material ($E_g > 3eV$), ZnO/Si heterojunction is expected to have a spectral responsivity that extend from NUV to NIR. Jeong [6] demonstrated a UV-enhanced ZnO/Si potodetector, he found that this detector exhibits strong responsivity of 0.5 and 0.3 A/W for UV 310 nm and red 650 nm photons, respectively. They also revealed that this detector shows a sign of reversal with a weak minimum near 380 nm. Doped ZnO films with other elements with different techniques have been reported by [7-9]. This work was focused on the morphological and I-V characteristic of Mg doped zinc oxide.

II. EXPERIMENTAL

A series of $Zn_{1-X}Mg_XO$ thin films with different Mg contents (x = 0, 0.1, 0.2, 0.3, 0.4) were deposited on a glass and silicon substrates by spray pyrolysis technique under ambient atmosphere.

The substrate temperature was set at ($400\,^{0}C$) during the film growth. Two kinds of aqueous solutions, Zinc acetate $Zn(CH_3COO)_2.2H_2O$ and Magnesium acetate $Mg(CH_3COO)_2.4H_2O$, were chosen as the sources of zinc and magnesium respectively.

The substrate used for $Zn_{1-X}Mg_XO$ /Si heterojunction is the commercially available monocrystalline n-type silicon wafer with (1.5-4 Ωcm) resistivity and $\langle 111 \rangle$ orientation with thickness of $(508 \mp 15)\mu m$. The surface of the Si wafer was already mechanically polished to mirror like surface. Native oxides were removed by 4:6 HF: H_2O solution. The wafer was cut into small pellets with appropriate size of about $(5\times 5mm^2)$.

The energy-dispersive X-ray analysis (EDX) and scanning electron microscope (SEM) were used to study some structural properties of $Zn_{1-X}Mg_XO$ thin films.

III. RESULTS AND DISCUSSION

III.1. Elemental analysis

The energy-dispersive X-ray analysis (EDX) spectra of the $Zn_{1-X}Mg_XO$ thin films deposited on a glass substrate at $(400\,^{0}C)$ by spray pyrolysis technique with different Mg-contents (x = 0, 0.1, 0.2, 0.3, 0.4) are shown in figures [(1)-(5)], which reveal that all the films contain the elements (Zn, Mg, O) as expected, indicating formation of $Zn_{1-X}Mg_XO$ thin films with high purity.

Fig.(1) shows the (EDX) spectra of the ZnO (pure) film and it reveals that the compound percentage for the (ZnO) and (C) are (92.41) and (7.59) respectively as listed in Table(1). Fig.(2) illustrates the (EDX) spectra of the $Zn_{0.9}Mg_{0.1}O$ film and it reveals that the compound percentage for the (ZnO), (MgO) and (C) are (89.70), (5.32) and (4.98) respectively. Fig.(3) shows the (EDX) spectra of the $Zn_{0.8}Mg_{0.2}O$ film with compound percentage for the (ZnO), (MgO) and (C) are (88.98), (6.33) and (4.69) respectively

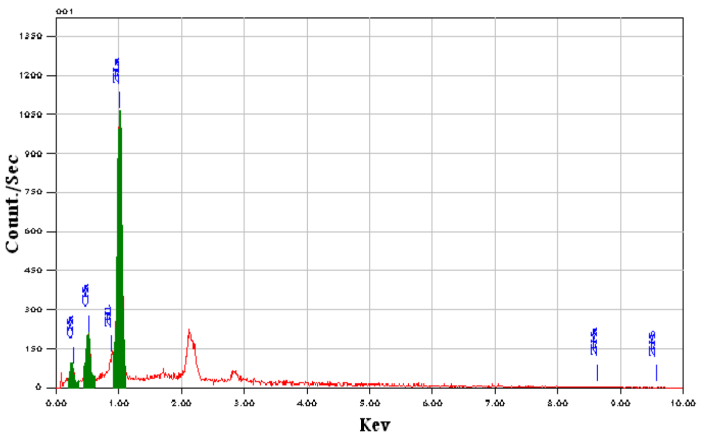

Fig. (1): EDX spectra of the ZnO thin film**.**

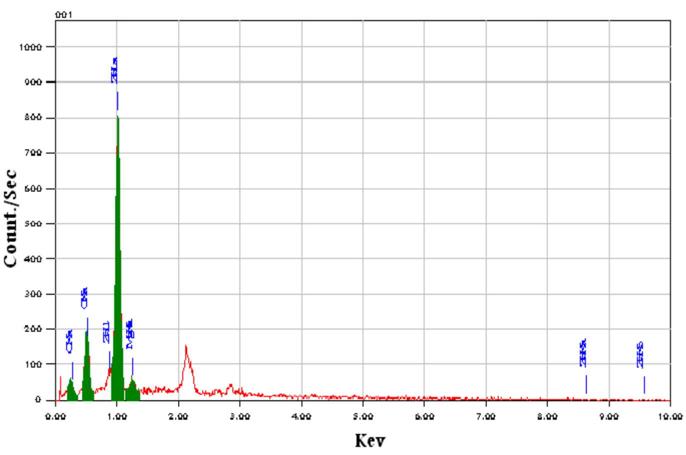

Fig. (2): EDX spectra of the $Zn_{0.9}Mg_{0.1}O$ thin film.

Fig.4 shows the compound percentages for (ZnO), (MgO) and (C) are (76.36), (17.10) and (6.54) respectively in $Zn_{0.7}Mg_{0.3}O$ film. Fig.5 depicts the (EDX) spectra of the

$Zn_{0.6}Mg_{0.4}O$ film with compound percentages for (ZnO), (MgO) and (C) of (71.15), (20.63) and (8.22) respectively.

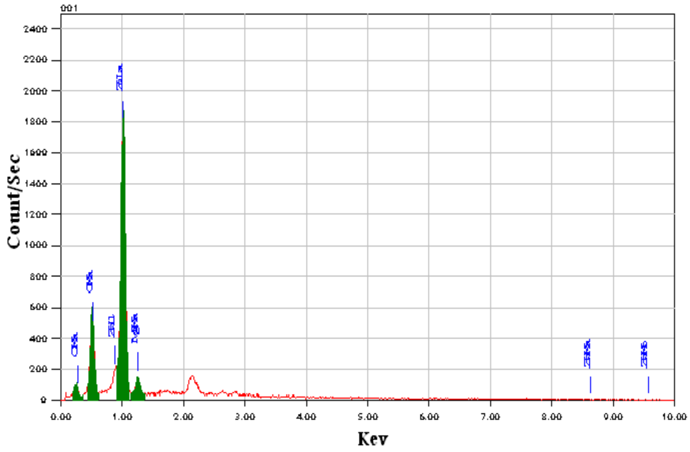

Fig. (3): EDX spectra of the $Zn_{0.8}Mg_{0.2}O$ thin film.

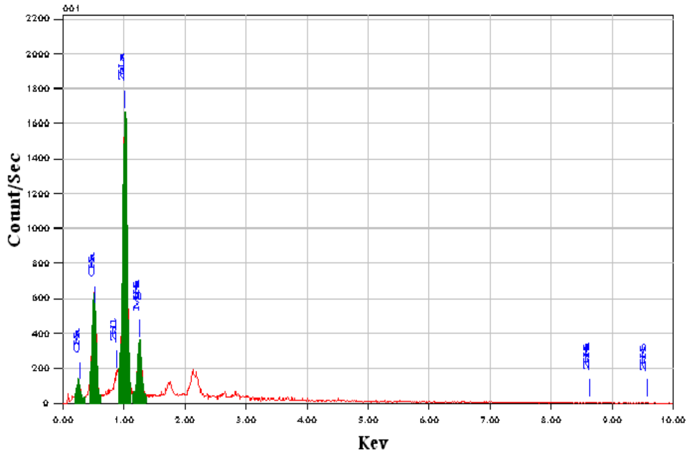

Fig. (4): EDX spectra of the $Zn_{0.7}Mg_{0.3}O$ thin film.

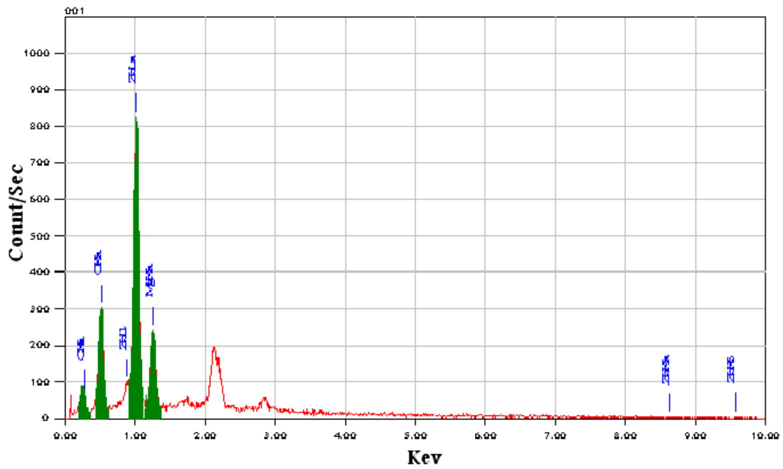

Fig. (5): EDX spectra of the $Zn_{0.6}Mg_{0.4}O$ thin film.

The other element (C) that is not expected to be in the deposited films, may resulted from the corning glass substrates or from the firing of some parts of layers of the deposited films during the growth process

Table (1): Compound percentages of the $Zn_{1-x}Mg_{x}O$ thin films

Mg-contents	Compound percentage (%)			Total
	C	ZnO	MgO	
0	7.59	92.41	0	100.00
0.1	4.98	89.70	5.32	100.00
0.2	4.69	88.98	6.33	100.00
0.3	6.54	76.36	17.10	100.00
0.4	8.22	71.15	20.63	100.00

III.2. Film thickness

Figures [6-10] show the cross-section SEM picture of the $Zn_{1-X}Mg_XO$ thin films deposited on a glass substrate at (400^0C) by spray pyrolysis technique. The thickness values of the films (400, 880, 696, 857 and 404) nm correspond to the Mg-concentrations (0, 0.1, 0.2, 0.3, 0.4) respectively.

Table (2) illustrates the difference in thickness which were measured by SEM and weighting methods.

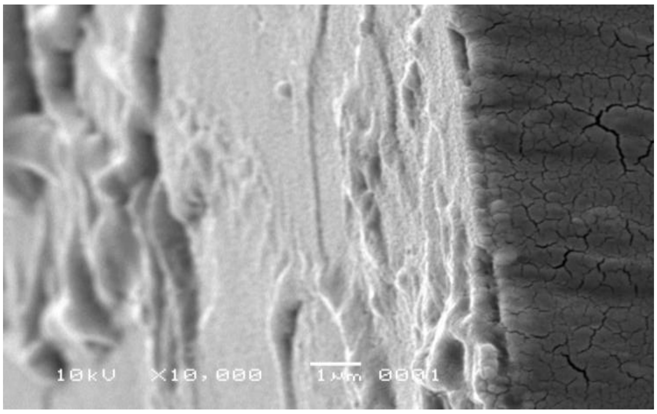

Fig. (6): The cross-section SEM picture of ZnO film.

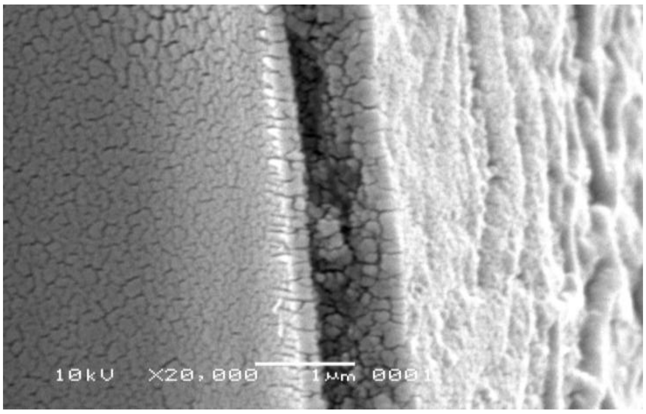

Fig. (7): The cross-section SEM picture of $Zn_{0.9}Mg_{0.1}O$ film.

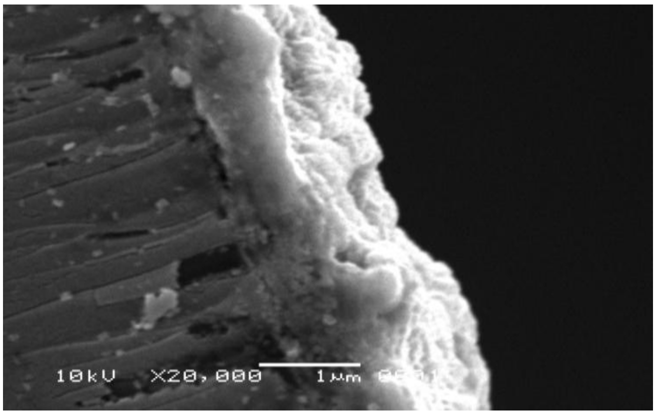

Fig. 8: The cross-section SEM picture of $Zn_{0.8}Mg_{0.2}O$ film.

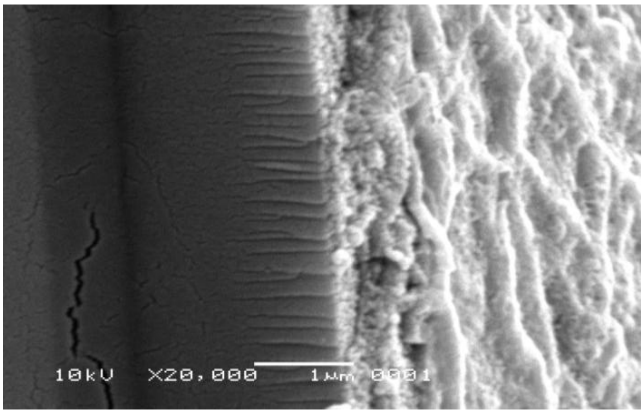

Fig. 9: The cross section SEM picture of $Zn_{0.7}Mg_{0.3}O$ film.

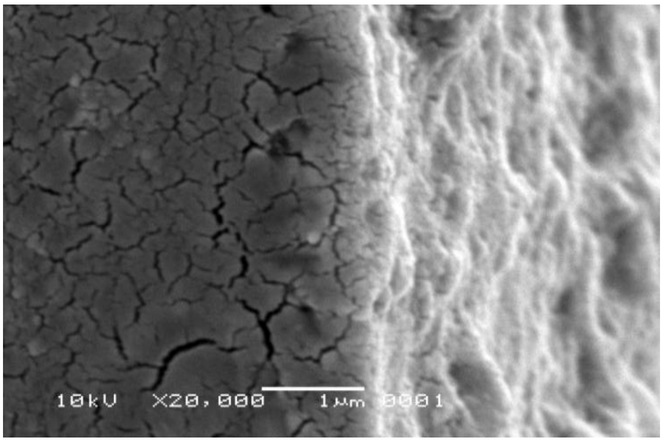

Fig. (10): The cross-section SEM picture of $Zn_{0.6}Mg_{0.4}O$ film.

Table (2): Comparison between the film thickness measured by SEM method and weighting method

Mg-contents	Film thickness (nm)	
	SEM method	Weighting method
0	400	536
0.1	880	644
0.2	696	700
0.3	857	729
0.4	404	695

III.3. Surface morphology

The surface morphology of the $Zn_{1-X}Mg_XO$ thin films deposited on a glass substrate at a substrate temperature (400^0C) by (SP) technique was examined by Scanning Electron Microscope (SEM) and the selected films, namely those with (x = 0, 0.1, 0.2, 0.3, 0.4) are shown in Figures [(11)-(15)].

A flat surface morphology of the ZnO film is obtained with the grain size equal to (71 nm), and a uniform distribution on the substrate is observed as shown in Fig.(11). It should be noticed that XRD results are related to the bulk of the sample, but SEM image analysis are related to a small section of the sample.

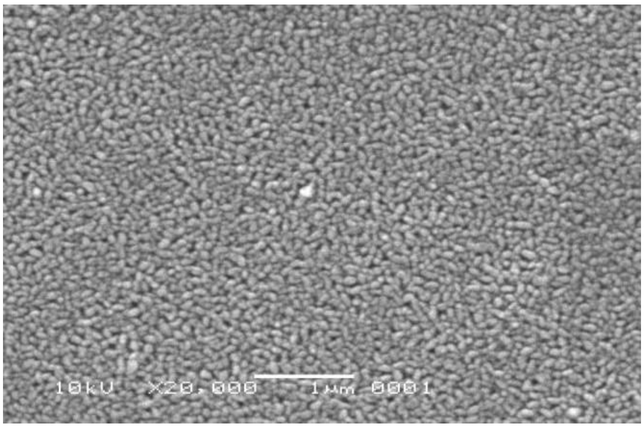

Fig.(11): SEM image of ZnO thin film.

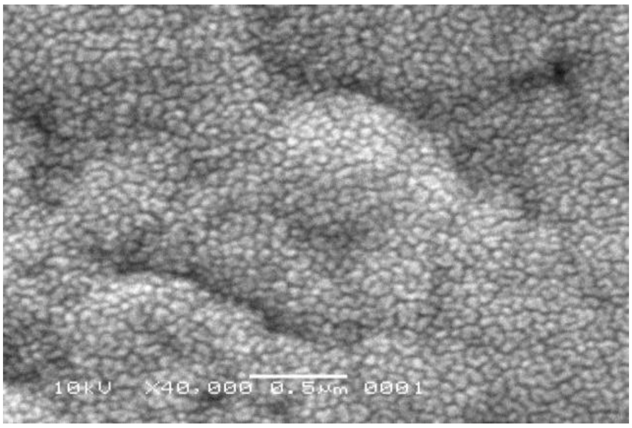

Fig.(12:) SEM image of $Zn_{0.9}Mg_{0.1}O$ thin film.

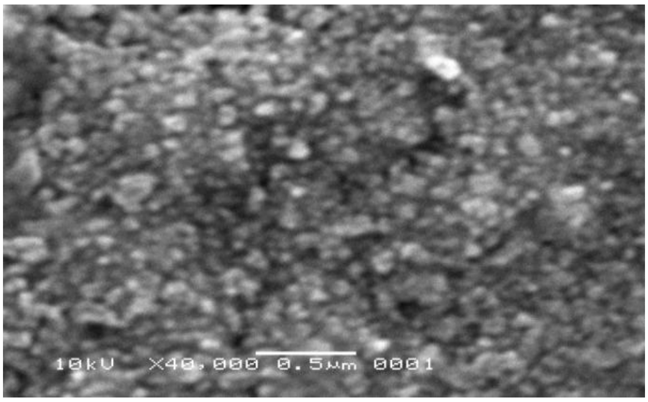

Fig. (13): SEM image of $Zn_{0.8}Mg_{0.2}O$ thin film.

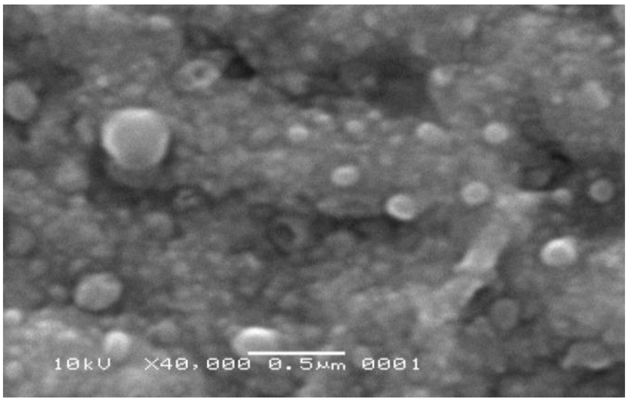

Fig. (14):SEM image of $Zn_{0.7}Mg_{0.3}O$ thin film.

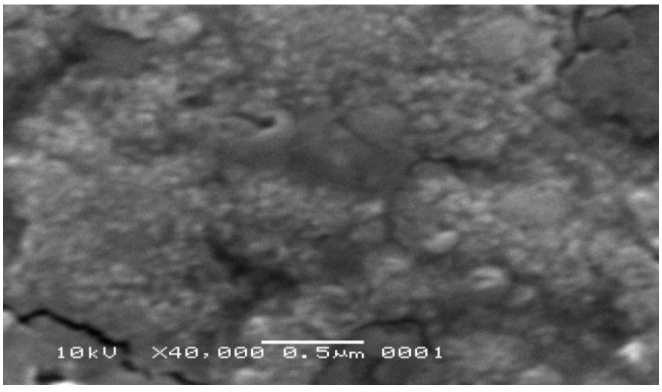

Fig.(15): SEM image of $Zn_{0.6}Mg_{0.4}O$ thin film.

Table (3) Comparison between the grain size estimated from (XRD) and (SEM) analysis.

Mg-contents	Grain size estimated from (XRD) (nm)	Grain size estimated from (SEM) images (nm)
0	34.247	59-83
0.1	16.767	35-59
0.2	23.606	47-71
0.3	20.875	47-59
0.4	17.837	35-47

With increasing Mg-contents in the films the surface morphology of the $Zn_{1-X}Mg_XO$ films becomes rough gradually as shown in Figs. [(12)-(15)]. From the (SEM) images the grain size values of the $Zn_{1-X}Mg_XO$ thin films deposited by (SP) technique are found to be in the ranges of (59-83)nm, (35-59)nm, (47-71)nm, (47-59)nm, (35-47)nm corresponding to the Mg-concentrations (x = 0, 0.1, 0.2, 0.3, 0.4) respectively. These values are bigger than that estimated from XRD results as shown in Table (3).

III.4. Characteristics of $Zn_{1-X}Mg_XO/n-Si$ heterojunction.

III.4.1 I-V Characteristic of $Zn_{1-X}Mg_XO/n-Si$ heterojunction.

Hall and Seebeck measurements revealed that pure ZnO (x=0) is n-type semiconductor and $Zn_{1-X}Mg_XO$ with concentrations (x = 0.1, 0.2, 0.3, 0.4) are p-type semiconductors, then, isotype n-n heterojunction will be obtained by ZnO/n-Si because both ZnO and Si semiconductors have n-type conductivity. Anisotype p-n heterojunction will be obtained by $Zn_{1-X}Mg_XO/n-Si$ for (x = 0.1, 0.2, 0.3, 0.4) because $Zn_{1-X}Mg_XO$ are p-type and Si is n-type. The I-V characteristics of $Zn_{1-X}Mg_XO/n-Si$ heterojunction are illustrated in figures [16-20] for dark and illuminated conditions. (I_d) is the current under dark condition, (I_t) is the current under illuminated condition and I_{ph} is the photocurrent ($I_{ph}=I_t-I_d$).

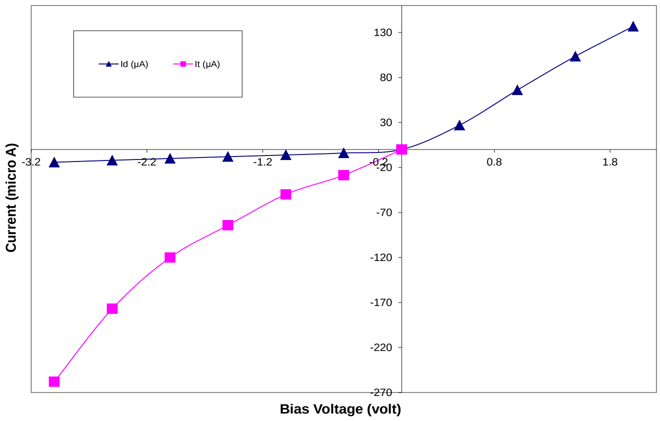

Fig. (16): I-V characteristic of ZnO/Si heterojunction under dark and illuminated conditions.

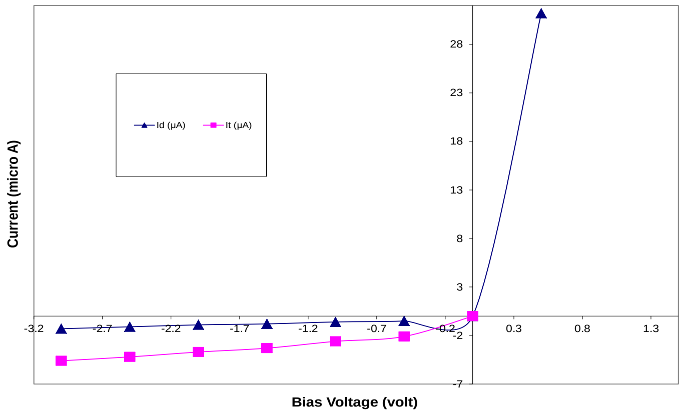

Fig. (17: I-V characteristic of $(Zn_{0.9}Mg_{0.1}O/n-Si)$ heterojunction under dark and illuminated conditions.

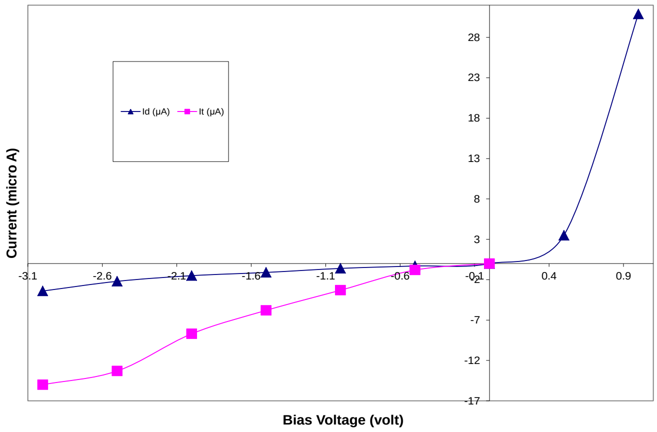

Fig. (18): I-V characteristic of $(Zn_{0.8}Mg_{0.2}O/n-Si)$ heterojunction under dark and illuminated conditions.

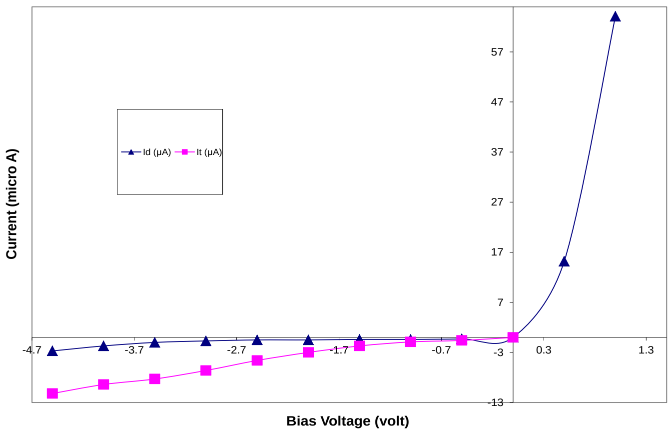

Fig. (19): I-V characteristic of $(Zn_{0.7}Mg_{0.3}O/n-Si)$ heterojunction under dark and illuminated conditions.

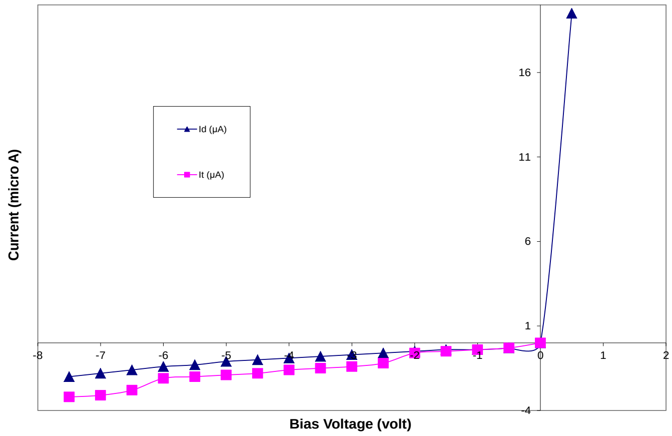

Fig. (20): I-V characteristic of $(Zn_{0.6}Mg_{0.4}O/n-Si)$ heterojunction under dark and illuminated conditions**.**

Table (4) Ideality Factor for $Zn_{1-X}Mg_XO/n-Si$ photodetectors.

Mg-contents	**Ideality Factor (B)**
0	29.55
0.1	11.08
0.2	16.02
0.3	12.07
0.4	10.91

We can clearly seen that the photocurrent (I_{ph}) decreases with the increasing of Mg-concentrations in the films, because, the optical bandgap of $Zn_{1-X}Mg_XO$ films increases with the increasing of Mg-content in the films.

From the Current-Voltage characteristics of $Zn_{1-X}Mg_XO/n-Si$ under dark condition we can calculate the ideality factor (B) by using the following classical [10] relation

$$B = \frac{q}{k_B T}\frac{V}{\ln \frac{I}{I_S}}$$

where (V) is the forward bias voltage, (k_B) is Boltzman constant and (I_S) is the saturation current.

The results show that the ideality factor values vary from (29.55) to (10.91) with different Mg-content in the films as illustrated in table (4).

III.4.2 Responsivity of $Zn_{1-X}Mg_XO/n-Si$ photodetectors for white light.

The responsivity values of $Zn_{1-X}Mg_XO/n-Si$ heterojunction detectors with different Mg-contents (x = 0, 0.1, 0.2, 0.3, 0.4), calculated by using [11] the relation $R = \frac{I_{ph}}{P_{in}}$ A/W are illustrated in Table (5). The Responsivity of $Zn_{1-X}Mg_XO/n-Si$ photodetectors decreases with increasing Mg-content measured for white light and bias voltage equals to (1, 2, 3 volts).

Table (5) Responsivity of $Zn_{1-X}Mg_XO/n-Si$ photodetectors for white light as a function of Mg-content and bias voltage.

Mg-content	Responsivity (A/W)		
	Bias = 1 volt	Bias = 2 volt	Bias = 3 volt
0	0.01752	0.044	0.09752
0.1	0.0008	0.00112	0.00132
0.2	0.00108	0.00288	0.00464
0.3	0.0002	0.0010	0.00236
0.4	0	0.00004	0.00028

Table (6) Lattice Mismatch between $Zn_{1-X}Mg_XO$ and Si.

Mg-Content	Lattice Mismatch %
0	50.25
0.1	50.20
0.2	50.06
0.3	50.08
0.4	50.05

The results show that the responsivity of $Zn_{1-X}Mg_XO/n-Si$ photodetectors for white light has reasonable values which indicates that the $Zn_{1-X}Mg_XO/n-Si$ photodetectors can be used as a detector that works in the visible and NUV span of the spectrum, this result is in good agreement with Al-Ani [12]. The results also show that the responsivity increases with increasing bias voltage as shown in Fig. (21).

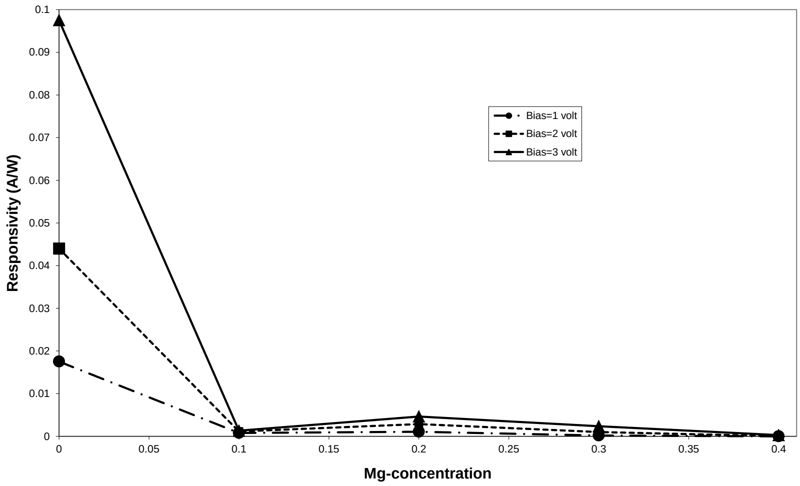

Fig. (21): Responsivity of $Zn_{1-X}Mg_XO/n-Si$ photodetectors for white light as a function of Mg concentration for different bias voltages.

Table (6) shows the lattice mismatch between $Zn_{1-X}Mg_XO$ and Si calculated by using [13] the following relation

$$Lattice \quad Mismatch = \frac{2|a_2 - a_1|}{a_2 + a_1} \times 100\%$$

where the lattice constant for Si equal to (a = 0.543 nm). The lattice mismatch was calculated to be about (50 %) for all the deposited films, this results are in good agreement with Al-Ani [12].

IV. CONCLUSION

$Zn_{1-X}Mg_XO$ thin films with high purity can be prepared by spray pyrolysis technique at a substrate temperature of $(400\,^0C)$. A flat surface morphology of the ZnO film is obtained with the grain size equal to (71 nm), and a uniform distribution on the substrate is observed. With increasing Mg-contents in the films, the surface morphology of the $Zn_{1-X}Mg_XO$ films becomes rough gradually this traced back to the difference in the lattice structure of ZnO and MgO. The ideality factor values vary from (29.55) to (10.91) with different Mg-contents in the films. The responsivity of $Zn_{1-X}Mg_XO/n-Si$ photodetectors for white light has high acceptable values, which indicates that the $Zn_{1-X}Mg_XO/n-Si$ photodetectors can be used as detectors in the visible and UV span of the spectrum.

References

[1] M. Joseph, H. Tabata, T. Kawai, "P- Type Electrical Conduction in ZnO Thin Films by Ga and N Codoping", Jpn. J. Appl. Phys. **38** , L1205-L1207 (1999).

[2] T. Yamamoto, H. Katayama-Yoshida, ”Physics and Control of Valence States in ZnO by Codoping Method Original Researh“, Physica B **302/303**, 155-162 (2001).
[3] A. Ohtomo, M. Kawasaki, ”Structure and Optical Properties of ZnO/$Mg_{0.2}$ $Zn_{0.8}$ O Superlattices”, Appl. Phy. Lett. **75**, 980-982 (1999).
[4] T. Makino, C.H. Chia, N.T. Tuan, H.D. Sun, ”Room-Temperature Luminescence of Excitons in ZnO/(Mg,Zn)O Multiple Quantum Wells on Lattice-Matched Substrates”, Appl. Phys. Lett. **77** , 975-977 (2000).
[5] D. Song, J. Zhao, A. Wang, P. Widenborg, W. Chin, A. Aberle, "Efficient ZnO/c-Si Heterojunction Solar Cell Prepared by Magnetron Sputtering" 17th European PV Conference, Munich, (2001), pp.1-4.
[6] S. Geong, "Study of diluted magnetic semiconductor: Co-doped ZnO", J. Appl. Phys. Lett., **81**, 4020-4022 (2002).
[7] Mohan Bahu, Kishor Kumar, Tanveer Bahu "CuO-ZnO Semiconductor Gas Sensor For Ammonia at Room Temperature", Journal of Electron Devices, **14**, 1137-1141 (2012).
[8] Arun Patil, Chandrakant Dighavkar, Ratan Borse, Shriram Patil, Rajendra Khadayate "Effect of Cr_2O_3 by Doping And Dipping On Gas Sensing Characteristics of ZnO Thick Films", Journal of Electron Devices, **15**, 1274-1281 (2012).
[9] Ziad T. Khodair, A. R. Alsrraf, M. I. Manssor, Nabeel A. Bakr "Synthesis and Study of ZnO Nanorods and Fe-Doped ZnO Nanoflowers by Atmospheric Pressure Chemical Vapor Deposition (APCVD) Technique", Journal of Electron Devices, **15**, 1200-1208 (2012).
[10] A. Georrgakilas, E. Aperathities, V. Foukaraki, M. Kayambaki, P. Panayotatos, "Investigation of the GaAs/Si Heterojunction Band Lineup with Capacitance and Current Versus Voltage Measurements", Material Science and Engineering, B **44**, 383-386 (1997).
[11] W. Budde, “Physical Detectors of Optical Radiation", Optical Materials Measurements **4**, Academic Press, New York, (1993).
[12] A. A. Al-Ani, "Preparing ZnO Film and Depositing it on Silicon by Spray Pyrolysis and Studying some of its Physical Properties", Ph.D thesis, University of Technology, (2006).
[13] B. L. Sharma and R.K. Purohit, "Semiconductor Heterojunction" Pergamon Press, New York (1974).