Structural, Surface Topography and Optical Characterization of Nanocrystalline \( \text{Mg}_x\text{Zn}_{1-x}\text{O} \) Thin Films Grown by Modified Chemical Bath Deposition (SILAR) Method

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Abstract. A series of \( \text{Mg}_x\text{Zn}_{1-x}\text{O} \) thin films were grown on glass substrates using modified chemical bath deposition (m-CBD) called successive ionic layer adsorption and reaction (SILAR) technique. The crystal structure, surface topography and the optical characterization of the prepared films were studied as a function of Mg/Zn \((x)\) content. It is observed that the deposited films have polycrystalline structure in nature and grown in two phases Hexagonal and cubic. The preferential orientation of the films was absorbed along (002) plane. Structural parameter such as crystallite size, number of dislocation density and micro-strain were also investigated. The crystallite size and surface roughness are increased with the increase of Mg\(^{2+}\) ions content. Thus the results showed that the surface topography and the surface quality of the deposited films can be controlled by Mg\(^{2+}\) ions content. The optical transmittance spectra analysis showed that transmittance increase with the increase \( \text{Mg}^{2+} \) content to about 85\% for \( x = 0.75 \), and the energy band gap increases (2.82 - 3.17) eV as the Mg\(^{2+}\) content increases \( x = (0.25 - 0.75) \). These results indicate that the \( \text{Mg}_x\text{Zn}_{1-x}\text{O} \) thin films can be potentially used in high-performance ultraviolet optoelectronic devices.

1. Introduction

\( \text{Mg}_x\text{Zn}_{1-x}\text{O} \) is an ideal material for UV detecting because of its high visible transparency and it possesses high UV absorption coefficients [1, 2]. \( \text{Mg}_x\text{Zn}_{1-x}\text{O} \) has two crystal structures, cubic rock salt and hexagonal wurtzite structure [3]. New studies have shown that the band gap of ZnO can be in the range, 3.32–4.50 eV by alloying with Mg [4, 5]. Therefore, it is an ideal material as a window/buffer layer in chalcopyrite-based solar cells to avoid window/buffer absorption losses [4, 5]. During the last few years, several physical deposition methods have been used for the deposition of \( \text{Mg}_x\text{Zn}_{1-x}\text{O} \) thin films such as RF reactive magnetron sputtering [6, 7], thermal evaporation [8], pulsed laser deposition [9, 10], ultrasonic spray pyrolysis [11], sol–gel method [12], plasma-assisted molecular beam epitaxy [13] and reactive electron beam evaporation (REBE) [14]. Moreover, as a semiconductor material, \( \text{Mg}_x\text{Zn}_{1-x}\text{O} \) has lately attracted significant interest because improvements in deposition mechanism made it possible to grow high-quality \( \text{Mg}_x\text{Zn}_{1-x}\text{O} \) thin films. In the present investigation, it has utilized simple and economical modified chemical bath Deposition (m-CBD) Successive Ionic Layer Adsorption and Reaction (SILAR) method to grow \( \text{Mg}_x\text{Zn}_{1-x}\text{O} \) thin films. SILAR procedure includes multiple successive dipping of the substrate in an anionic and cationic solution, which is simple, flexible, and economical and offers an easy way to dope semiconductor films. It does not require high-quality substrates and operate at room temperature without need of a vacuum. The wastage due to bulk precipitations in the solution can be avoided by using this method. In the present work the effect of Mg\(^{2+}\) ions content \((x)\) regarding their structural, morphological and optical properties of \( \text{Mg}_x\text{Zn}_{1-x}\text{O} \) thin films deposited on glass substrates by (m-CBD) SILAR method was investigated.
2. Experimental details

2.1. Materials
The chemical reagents used in the experiment were of analytical grade. Magnesium sulfate (MgSO$_4$) and Zinc Sulfate Heptahydrate (ZnSO$_4$.7H$_2$O) and sulfuric acid (H$_2$SO$_4$) were purchased from Sigma–Aldrich Co. Ammonium hydroxide (NH$_4$OH) and acetone (CH$_3$COCH$_3$) were purchased from Merck KGaA.

2.2. Synthesis of MgxZn1−xO thin films by SILAR method
The deposition of Mg$_x$Zn$_{1-x}$O thin films onto glass substrates by SILAR method can be described as follows: at first, substrates were cleaned by three steps which are cleaning in dilute sulfuric acid solution (H$_2$SO$_4$:H$_2$O, 1:5, v/v), in absolute acetone and in double distilled water for 10 min each in an ultrasonic bath. Two aqueous solutions with 0.1M concentration were prepared by dissolved 1.203g of MgSO$_4$ and 2.87g of ZnSO$_4$.7H$_2$O in 100 ml of double distilled water (DDW) for each one respectively. The solution were stirred in a magnetic stirrer for 1 hour at room temperature in order to get transparent and well-dissolved solutions. The two solutions were mixed in different (x)% and (1-x)% volumetric content from the total volume of the mixed solution with stirring, and the pH value of the mixed solution was adjusted to 7.5 by adding ammonium hydroxide (NH$_4$OH) drop wise. The mixed solutions were heated up to 85 °C and the substrate was dipped into the mixed solutions (as a source of Mg and Zn cations) for 15s the cations were adsorbed on the substrate surface. Then, the substrate was rinsed into DDW at 85 °C for 15s to remove weakly adsorbed ions. The above process represents one cycle and produce one coating of Mg(OH) and Zn(OH) film on the substrate. This cycle was repeated for 15 times to have well adherent film of thickness around 150 nm. To investigate the effects of Mg$_2^+$ concentration (x) on the films, three series of samples x = (0.25, 0.5, 0.75) % were produced, where the (1-x) Zn concentration in the films was (0.75, 0.5, 0.25)% respectively. Finally, the glass substrates with the deposited MgxZn1-xO films were cleaned ultrasonically in order to remove excess unadherent ions on the substrate and were annealed at 450°C for 1 hour in muffle furnace, in order to convert Mg(OH) and Zn(OH) into MgZnO with evaporation. The color of the films became white after annealing.

2.3. Characterization
Structural, surface morphology and Optical properties of the deposited films were investigated, using x-ray diffractometer (XPert Pro MPD PANalytical) Cu kα radiation with a wavelength of 1.5406 Å, the current 30 mA, voltage 40 kV, and scanning angle varied in the range of 20 to 80º. Whereas the surface morphology were studied using atomic force microscope CSP model AA3000 AFM supply by Angstrom. The Optical properties were studied using UV-Vis spectrometer Mega 1200 Sinco in the wavelength range 200-1100 nm.

3. Results and discussion

3.1. Structure properties
The XRD spectra of prepared Mg$_x$Zn$_{1-x}$O thin films are recorded in Figure 1. Most of the peaks assigned to H(002),H(101), H(102) and H(201), orientations of the hexagonal (wurtzite) phase of ZnO as well as the peaks C(111), C(200) and C(220) orientations of phase cubic (rocksalt) of MgO. The intensity of (002) of XRD patterns for Mg$_x$Zn$_{1-x}$O was significant decreases and shifts towards high 20 angles with the Mg$_2^+$ content increases due to the effect of Mg$_2^+$ content in ZnO thin films. This outcome suggests that the lattice parameter along the c-axis decreases indicating a compressive strain [1]. The distinguish peaks of all Mg$_x$Zn$_{1-x}$O thin films match well with standard data (JCPDS 43-1022) for MgO and (JCPDS 36-1451) for ZnO. This result is in good agreement with almost all previous studies [11, 12, 15].
The lattice parameters (a) and (c) for hexagonal planes of the Mg$_x$Zn$_{1-x}$O thin films were calculated from the following equation [16]:

$$\frac{1}{d^2_{hkl}} = \frac{4}{3} \left( \frac{h^2 +hk +k^2}{a^2} + \frac{l^2}{c^2} \right)$$

Where $d$ is the interplanar spacing of given miller indices $h$, $k$ and $l$. (a) and (c) values were in a good agreement with the (JCPDS 43-1022) card data and shown in table (1).

The values of lattice constant $a$ and $c$ of Mg$_x$Zn$_{1-x}$O thin films observed with the Mg$^{2+}$ incorporation are decreases because the ionic radius of Mg$^{2+}$ (0.57 Å) was slightly smaller than that of Zn$^{2+}$ (0.60 Å).

The crystallite size has been determined by using the Scherrer's formula [17]:

$$D = \frac{0.9\lambda}{Bc\cos\theta}$$

Where $\lambda$ is the wavelength of the x-ray, $\theta$ is Bragg angle and $B$ is the FWHM (full width at half maximum) value in radian. The crystallite size is observed increased from 25.16 nm to 61.45 nm and then decrease to 38.35 nm with increase in Mg$^{2+}$ composition. This is probably indicating that Mg$^{2+}$ content is contributing to the change in crystallinity as well as the preferred growth orientation of Mg$_x$Zn$_{1-x}$O thin films and the crystallite size confirm the nanostructure property of the as deposited and doped thin films as shown in table(1).

The dislocation density ($\delta$) of Mg$_x$Zn$_{1-x}$O thin films is defined as the number of dislocation lines per unit volume and determined from the relation [18, 19]:

$$\delta = \frac{1}{(D)^2}$$

Figure 2 shows $\delta$ and N as a function of Mg$^{2+}$ concentration of Mg$_x$Zn$_{1-x}$O thin film, it is absorbed $\delta$ increasing with the increasing of Mg$^{2+}$ concentration. Thus the results show that Mg$^{2+}$ content increase reduces the dislocation density of the thin films.

The number of crystallites per unit surface area (N) could be calculated according to [20]:

![Figure 1: The x-ray diffraction patterns of Mg$_x$Zn$_{1-x}$O thin films, as a function of Mg$^{2+}$ concentration, the peaks marked with (*) and (#) are refer to MgO and ZnO respectively.](image-url)
Where \( t \) is the thickness of the film, it is absorbed that \( N \) increased with the increase of \( \text{Mg}^{2+} \) concentration). The calculated values of \( \delta \) and \( N \) with respect to the \( \text{Mg}^{2+} \) concentration were shown in table 1. The micro-strain \((\varepsilon)\) has been determined using the following equation [19, 20]

\[
Micro - Strain \ (\varepsilon) = \frac{B \cos \theta}{4} \quad (5)
\]

Figure 3. shows the micro-strain \((\varepsilon)\) of \( \text{Mg}_{x}\text{Zn}_{1-x}\text{O} \) thin films for (002) plane, it is initially increased from (5.68) to (8.5) and then decreased to (3.41) with increase of \( \text{Mg}^{2+} \) concentrations due to the ionic radius of \( \text{Zn}^{2+} \) ions which is slightly higher than \( \text{Mg}^{2+} \) ions, the strain in ZnO lattice is influenced by \( \text{Mg}^{2+} \) and thereby alters the preferential growth.

### Table 1. Structural parameters of \( \text{Mg}_{x}\text{Zn}_{1-x}\text{O} \) thin films obtained from XRD data.

| Compound    | 20 (hkl) | FWHM Deg | \( a \) (Å) | \( c \) (Å) | Crystal Size (nm) | Dislocation Density \((\delta) \ 10^5 \) Lines/m² | \( N \) \( 10^{16} \) m⁻² | Micro Strain \((\varepsilon)\) \( 10^{-3} \) |
|-------------|---------|----------|-----------|-----------|-------------------|-----------------------------------|-------------------|------------------|
| \( \text{Mg}_{0.25}\text{Zn}_{0.75}\text{O} \) | 34.11 H(002) | 0.1574 | 2.89 | 5.24 | 38.35 | 0.70 | 2.65 | 5.681 |
|             | 35.801 H(101) | 0.4723 |            |          |                   |                                   |                   |                  |
|             | 36.855 C(111) | 0.0886 |          |          |      2.97 |        4.36 |       61.45 | 2.64 | 6.46 | 8.503 |
|             | 66.383 H(201) | 0.0960 |          |          |                   |                                   |                   |                  |
|             | 34.40 H(002) | 0.2362 |          |          |                   |                                   |                   |                  |
| \( \text{Mg}_{0.5}\text{Zn}_{0.5}\text{O} \) | 35.51 H(101) | 0.0886 | 2.97 | 4.36 | 61.45 | 2.64 | 6.46 | 8.503 |
|             | 43.181 C(200) | 0.0787 |          |          |                   |                                   |                   |                  |
|             | 47.34 H(102) | 0.0590 |          |          |                   |                                   |                   |                  |
|             | 63.296 H(220) | 0.3149 |          |          |                   |                                   |                   |                  |
| \( \text{Mg}_{0.75}\text{Zn}_{0.25}\text{O} \) | 34.180 H(002) | 0.9446 | 2.80 | 5.21 | 25.16 | 1.6 | 8.93 | 3.41 |
|             | 36.84 C(111) | 0.0689 |          |          |                   |                                   |                   |                  |
|             | 43.897 C(200) | 0.0590 |          |          |                   |                                   |                   |                  |
|             | 47.368 H(102) | 0.0590 |          |          |                   |                                   |                   |                  |
|             | 62.919 H(220) | 0.0720 |          |          |                   |                                   |                   |                  |
|             | 66.687 H(201) | 0.1440 |          |          |                   |                                   |                   |                  |
Figure 2. The variation of (δ) and (N) of Mg\textsubscript{0.7}Zn\textsubscript{0.3}O thin films as a function of Mg\textsuperscript{2+} concentration for (002) plane.

Figure 3. The variation of the micro-strain (ε) of Mg\textsubscript{x}Zn\textsubscript{1-x}O thin films, as a function of Mg\textsuperscript{2+} concentration for (002) plane.

Figure 4. shows AFM images of Mg\textsubscript{x}Zn\textsubscript{1-x}O thin film. It can be seen that all the samples have uniform surfaces and dense grains. The surface roughness is observed increasing from (20.9 to 31.2) nm and then decreasing to 32.8 nm with an increase in Mg\textsuperscript{2+} composition, shown in the table (2). The variation in the RMS roughness is attributed to the partial padding of Mg in the pores. From the (results above), it is seen clearly an improvement of the microstructure and the crystalline quality of the Mg\textsubscript{x}Zn\textsubscript{1-x}O composite as the Mg\textsuperscript{2+} content increased. This result is in good agreement with [21]. The average grain size of the Mg\textsubscript{x}Zn\textsubscript{1-x}O sample was increase from (89 to 100) nm with increase in Mg\textsuperscript{2+} content. The value that is larger than that obtained from the calculated via Scherrer’s formula by XRD and found to be from (25 to 61) nm with increase in Mg\textsuperscript{2+} content. These findings were attributed to line broadening mechanisms, other than grain size, such as stress and defects [22]. The average grain diameter values of all compositions x for Mg\textsubscript{x}Zn\textsubscript{1-x}O thin films gives an indicate that the prepared films were a nanocrystalline and their potential in high-performance deep ultraviolet optoelectronic devices [22].
Figure 4. AFM images of Mg$_x$Zn$_{1-x}$O thin films, a function of Mg$^{2+}$ concentration (x) a: 0.25, b: 0.50 and c: 0.75.

Table 2. The optical band gap, RMS and grain size for AFM image of Mg$_x$Zn$_{1-x}$O thin films.

| Compound     | Band gap (eV) | Transmittance (%) | Roughness Average nm | Root mean square nm | Grain diameter AFM |
|--------------|---------------|-------------------|----------------------|---------------------|--------------------|
| Mg$_{0.25}$Zn$_{0.75}$O | 2.82          | 70                | 20.9                 | 25                  | 89                 |
| Mg$_{0.5}$Zn$_{0.5}$O    | 2.94          | 62                | 31.2                 | 39.1                | 91                 |
| Mg$_{0.75}$Zn$_{0.25}$O | 3.17          | 59                | 23.8                 | 28.3                | 100                |
3.2. Optical properties

Figure 5. shows the absorption coefficient spectra of the deposited $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ thin films with (0.25, 0.5 and 0.75) $\text{Mg}^{2+}$ concentrations, respectively. The absorption edge of the films were observed to shift towards lower wavelengths (blue shift) with respect to the enrichment of $\text{Mg}^{2+}$ concentration, the blue shift can be related to the fundamental absorption edge of MgO which shifted the absorption edge of $\text{ZnO}$ towards low wavelength with increase of $\text{Mg}^{2+}$ ion concentration. The absorption studies revealed that the fabricated films are more suitable for the fabrication of deep ultraviolet optoelectronic devices.

![Absorption Coefficient Spectra](image)

**Figure 5.** The Absorption Coefficient spectra of $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ thin films, as a function of $\text{Mg}^{2+}$ concentration.

The difference of transmittance against wavelength for different composition $x$ of the $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ is presented in Fig.6. It was observed that transmittance increased with the increase of the $\text{Mg}^{2+}$ content in the $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ thin films. The transmittance varied from 59% to 70% as $x$ varies from 0.25 to 0.75 in the 350–800 nm range due to evidencing the substitutional incorporation of $\text{Mg}^{2+}$ into the $\text{Zn}^{2+}$ site of the wurtzite lattice. These results correspond well with those in other papers [23].

In a direct band gap semiconductor such as $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ thin film, the absorption coefficient is related to the incident photon energy by the following relation [24]:

$$\alpha_{\text{MgZnO}} = A(h\nu - E_{\text{gMgZnO}})^\beta$$  \hspace{1cm} (6)

Where $\alpha_{\text{MgZnO}}$ are the absorption coefficients of $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ thin films, $h\nu$ is the energy of the incident photon, is (0.5) for a direct transition semiconductor, and $E_{\text{gMgZnO}}$ are band gap energies $\text{Mg}_x\text{Zn}_{1-x}\text{O}$, respectively.
The optical energy gap ($E_g$) of the prepared films can be obtained by plotting $(\alpha h\nu)^2$ versus $(h\nu)$ extrapolating the straight line portion of this plot to the energy as in Figure 7. The energy band gap ($E_g$) of Mg$_x$Zn$_{1-x}$O thin films were increased from 2.82 eV to 3.17 eV by tuning the incorporation of Mg$^{2+}$ ions. This increase can be attributed to the position of absorption edge of MgO at higher energy comparing with the position of ZnO absorption edge, which shifted towards higher energies with the increase of Mg$^{2+}$ ions concentration in the films. Also the widening in band gap can be attributed to the well-known Burstein–Möss effect or (B.M shift) [24] and/or to the forming of hexagonal Mg$_x$Zn$_{1-x}$O alloy phase [15, 25]. These results are in agreement with the results obtained by [15, 25].
Figure 7. The optical energy band gap (E_g) of Mg_xZn_1-xO thin films, as a function of Mg^{2+} concentration.

The increase of band gap can prevent the window absorption losses. The nature of this variation in the band gap energy may be useful to design a suitable window material in the fabrication of many optoelectronic devices such as missile warning and tracking, chemical/biological agent detecting and in other optoelectronic devices. [20]. The variation of energy band gap with different Mg^{+} contents of deposited Mg_xZn_1-xO thin films in this paper were given in table 2.

4. Conclusions
Mg_xZn_1-xO thin films had been deposited by SILAR method and annealing at 450° C on glass substrates. The XRD studies of the prepared films showed polycrystalline hexagonal and cubic phase with a preferred orientation along (002) plan and there is a slightly shifted to the larger 2θ angle. The AFM image shows, Mg^{2+} content greatly influences the surface morphology of Mg_xZn_1-xO films, and an increase of Mg^{2+} content is increasing the crystallite size and surface roughness. The crystal size values of all (x compositions) for Mg_xZn_1-xO thin films give an indicate that the prepared films were a nanocrystalline and their potential in high-performance deep ultraviolet optoelectronic devices. Increase of dislocation density and micro-strain were obtained with increase of Mg^{2+} content. The optical studies show that the deposited films have high transmittance in the visible region more than 70%. The absorption edges of the Mg_xZn_1-xO films had been shifted towards lower wavelengths (blue shift) as respect to the increase of Mg^{2+} concentration. The band gap of Mg_xZn_1-xO thin films had been increased when the Mg/Zn mole ratio was increased. This behavior is related to Burstein–Möss effect which served as a supportive tool in explaining the observed band gap widening associated with Mg^{2+} concentration. However, the reflectance shifted towards the lower wavelength with increasing Mg^{2+} value. Finally, the optical properties of Mg_xZn_1-xO vary considerably with change in the Mg^{2+} concentration.

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