Synthesis and Characterizations of ZnO Thin Films Grown by Physical Vapor Deposition Technique

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Abstract

In the current study, Zinc oxide (ZnO) thin films have been synthesized over the whole the glass-slide substrate by utilizing the physical vapor deposition (PVD) technique. The Zinc (Zn) seed layer was deposited by heating the high purity Zn powder by using a molybdenum (Mo) boat at 37.503×10^{-3} Torr vacuum pressure of the PVD chamber. The ZnO thin films were fabricated by oxidation of the Zn seed layer coated glass-slide substrate at 400 ˚C. The morphological, chemical compositions, crystal quality, structural and optical properties of fabricated ZnO thin film were characterized and studied utilizing several characterization techniques. The results found that the high distribution density, homogenous, uniform, and high-quality ZnO thin film was grown over the entire substrate. The synthesized ZnO thin film with a thickness of 130 nm was grown with high purity and polycrystalline hexagonal-Wurtzite phase of ZnO. The sharp, and dominant diffraction peak was observed at peak position 34.3375 along (002) plane and c-axis. The investigated crystal size, dislocation density, and interplanar spacing were about 13.33 nm, 5.63×10^{-5} A°, and 2.609 A°, respectively. Also, UV-visible spectroscopy results show the high transmittance and low absorbance in the visible (Vis.) region and were about 90%, and the transmittance decreases sharply near the UV region at a wavelength around 383 nm. Besides, obtained the energy band-gap (E_g) was about 3.24 eV.

I. INTRODUCTION

The fabrication, examination, and characterization of Zinc Oxide (ZnO) thin film have been an active and functional field of different research for decades [1]. Recently, many scientists and researchers have been extensively studied and worked on the wide energy gap semiconductor materials includes ZnO due to their excellent properties and uses in optoelectronic (OPE) devices [2]. The ZnO has a hexagonal wurtzite structure and direct optical energy gap which is 3.37 eV at room temperature (RT) [3-6]. At RT, the ZnO has the wider and larger exciton binding energy which is 60 meV compared to the Gallium Nitrate (GaN) which is (20 meV) [4, 7]. Also, ZnO has a high chemical, thermal, and electrical stability [8]. The crystal growth of ZnO can be grown by using simple fabrication technology which is the other benefit of ZnO [9]. Therefore, it can say that zinc oxide is highly interesting for several areas of very high technological implementations and manufacturing [2].

The zinc oxide thin films have been emerged very interesting due to their excellent implementations, as the window layer (WL) in solar cell system, and as the transparent conducting-oxide (TCO) [10, 11]. Due to the very high optical transmittance (T) in the visible (Vis.) region and an excellent piezoelectric (PE) characteristic, several another uses of ZnO thin films includes the surface acoustic wave device, and the film bulk acoustic resonator filter (FBARF)have also studied and investigated [12, 13]. The zinc oxide thin films have been prepared and synthesized by using different physical and chemical methods and techniques [14]. These methods include the chemical bath deposition method (CBD), pulsed laser

deposition (PLD), molecular beam epitaxy (MBE), radio frequency (RF) magnetron sputtering technique, physical vapor deposition (PVD) technique, metal-organic chemical vapor deposition (MO-CVD), spray pyrolysis (SP), sol-gel method, hydrothermal method, an ultrasonic spray method [15-18]. Notwithstanding, the PVD technique is a very simple, low-cost, reproducible, and easy technique that can be utilized and scaled up for the synthesis of a large range and types of different ZnO nanostructures such as nanorings, nanohelixes, nanowires, nanoparticles, nanobelts, thin films, nanorods, and nanoneedles [19].

In this work, an easy and simple physical vapor deposition (PVD) technique with 37.503×10^{-3} Torr vacuum pressure of the PVD chamber. was used to deposit the ZnO thin films on the glass substrates. The morphological, chemical compositions, crystal quality, structural and optical properties of fabricated ZnO thin film were characterized and studied utilizing several characterization techniques.

II. EXPERIMENTAL DETAILS

In this work, all utilized beginning materials such as Zinc (Zn) powder, and Ethanol (C_2H_6O) purchase from the Company of Sigma-Aldrich without further purification. The distilled-water (DW) has been utilized for remedies and synthesis processes. The microscopic glass slide was employed as the substrates for zinc oxide thin film deposition. Before the deposition process of ZnO thin film, the glass substrates were prepared with a dimension of $(25 \times 75 \times 1)$ mm^3. The glass-slide substrates were cleaned by soaking the glass substrates in the solution of in Chromic Acid (H_2CrO_4) for 1 day, and then taken off from the acid solution and rinsed with distilled water, and Ethanol (C_2H_5OH) for 15 min, respectively. Besides, the glass substrates have been cleaned ultrasonically with distilled water for 15 min, and dried in air at room temperature, and kept in a desiccator [20]. The mentioned cleaning process provides good adhesion, growth nucleation center, and uniform synthesis of thin films [21]. The 130 nm thickness of ZnO thin film was synthesized by using a one-step PVD technique. The PVD deposition process was carried out by evaporating the 137.32 mg of high purity (99.6%) Zinc (Zn) powder on the whole cleaned glass-slide substrates by utilizing the molybdenum (Mo) boat to heat the Zn powder. The vacuum pressure was 37.503×10^{-3} Torr of the PVD chamber. Also, the glass-slide substrates have been rotated during PVD evaporating process by using a uniform rotating substrates holder that holds the 12 glass substrates samples. After finishing the PVD synthesis process of Zn thin film, the deposited the Zn upon the substrates were bring out of the PVD chamber and transferred into the laboratory annealing furnace at 400°C for 1.5 h to get the ZnO thin films. A schematic diagram for the synthesis of ZnO thin film is shown in Figure (1).

The surface morphological properties, chemical composition, crystal quality, and structural properties of synthesized ZnO thin film have been characterized and studied by utilizing the field-emission scanning electron microscopy (FE-SEM) (SEM 4500-Quanta), energy-dispersive X-ray (EDX) analysis, and analytical (XRD) X- Pert PRO (Cu Kα = 1.5406 A˚ at 40 kV, 30 mA) in the 2θ range of (20˚ to 70˚) with the rate of scanning was 1°/ min, respectively.
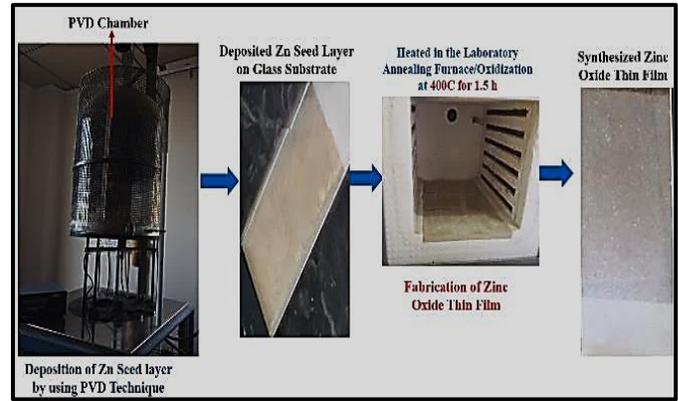

Fig. 1. Schematic Diagram of Synthesized ZnO Thin Film

The optical properties, optical transmittance spectrum, and energy band gap of the ZnO thin film was studied by utilizing the ultraviolet (UV-Vis.) spectrophotometer in the range of (300–1000) nm. The interplanar distance (d) of the synthesized ZnO thin film along diffraction peak (002) has been calculated by using Bragg's law [22]:

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

Where *a*, *c* and hkl are the lattice parameters constants, and miller indices, respectively.

The average crystal size (D) and the number of defects which is called the dislocation density (δ) of the deposited ZnO thin film along (002) diffraction peak was obtained using Scherrer's equation [23]:

$$D = \frac{k\lambda}{\beta \cos\theta} \qquad (2)$$

$$\delta = \frac{1}{D^2} \qquad (3)$$

Where D, δ , θ, k, β, and λ are the average crystal size, dislocation density, diffraction Bragg's angle, constant which is equal to 0.9, full width at half maximum (FWHM), and wavelength of the X-ray source which is equal to 1.54050 Angstrom, accordingly.

The energy band gap energy (Eg) of synthesis ZnO thin film

$$(\alpha h\nu)^2 = A(h\nu - E_g)^n \qquad (4)$$

was calculated from the Tauc's relation [24, 25].

Where α, hν, A, Eg, and n are the absorption coefficient, the photon energy, constant, the optical band gap energy and depends on the transmission type (n= 2 for indirect transmission and n= (1/2) due to direct transmission of ZnO). The α coefficient was determined by [26].

$$\alpha = \frac{\ln(\frac{1}{T})}{d} \qquad (5)$$

Where (T and d) are the transmittance and thickness of synthesized ZnO thin film sample.

III. RESULTS AND DISCUSSION

The ZnO surface topography top-view of the synthesized ZnO thin film with different magnifications using FESEM analysis are shown in Figure 2. It can be seen that the homogenous, uniform, high distribution density, and high-quality thin film of ZnO was deposited over the whole substrate. For a deep investigation of ZnO thin film morphology, the synthesized ZnO sample was characterized by using energy dispersive X-ray (EDX) analysis as shown in Figure 3 (a). The EDX spectrum of the deposited ZnO thin film sample was taken for the FESEM characterizations which indicated that the ZnO thin film sample produced through the PDV technique had a clean phase of ZnO. From Figure 3 (a), the EDX analysis of the ZnO thin film indicated that the fabricated ZnO thin film sample contained zinc (Zn), and oxygen (O). The EDX spectrum showed one robust peak for Zn around 1 keV correspondingly and a singular peak for oxygen at ~0.5 keV, which is typical for ZnO thin films [27]. The high intensity of Zn and O peaks displayed that the synthesized thin film sample was mostly ZnO. Figure 3 exposed that the produced ZnO thin film sample possessed 80.74% Zn weight (Wt) percent associated with only 19.26 % O weight percent reveal nearly 3.7:1 ratio for Zn and O, respectively. These obtained values of Zn and O are in good coincides with the theoretically expected stoichiometric Wt % of Zn and O, i.e., 80.3% and 19.7% respectively [28]. Accordingly, the EDX analysis emphasizes that the ZnO thin film deposited by the PVD technique possessed high purity elemental composition. Besides, the atomic % of Zn was 50.64% accompanied by 49.34% for O atomic percent giving roughly a 1:1 ratio for Zn and O, in this order. Further details regarding to the distributions and the elemental mapping of Zn and O elements are shown in Fig.4 (b).
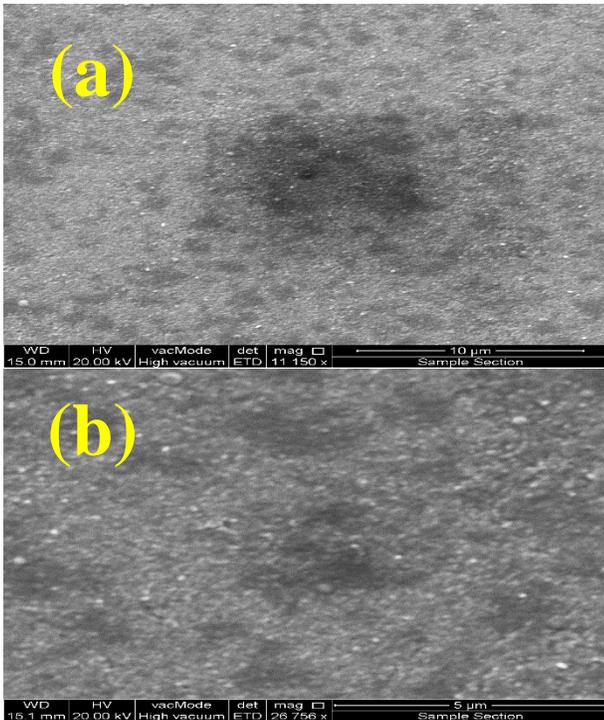

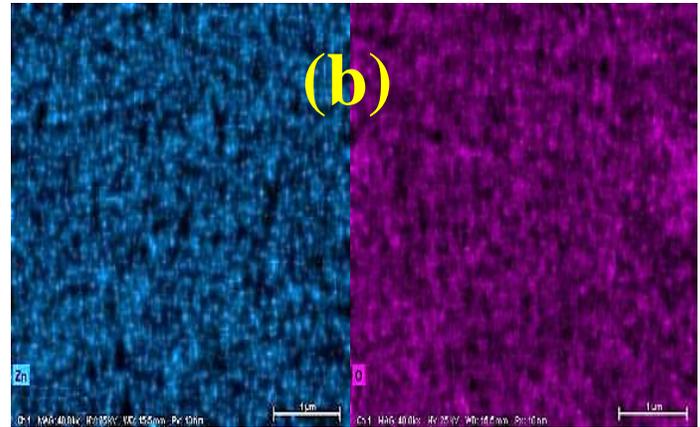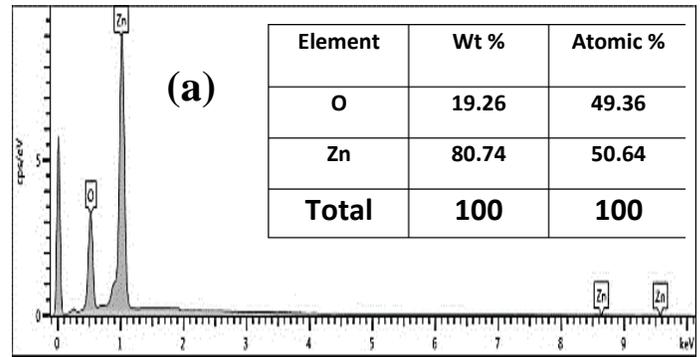| Element	Wt %	Atomic %
O	19.26	49.36
Zn	80.74	50.64
Total	**100**	**100**

Fig. 3. (a) The EDX Spectrum Analysis of the synthesized ZnO Thin Film. (b) Elemental Mapping analysis for 3.7 Zinc:1Oxygen wt.% ratio for ZnO Thin Film Synthesized by using PVD Technique.

Fig. 2. Surface Morphology (Top-View) FESEM Image of Synthesized ZnO Thin Film (a) low Magnification and (b) High Magnification

The X-ray diffraction (XRD) pattern of ZnO thin film deposited using the PVD technique is demonstrated in Figure 4. From the XRD pattern, it can investigate that all the diffraction peaks in all XRD patterns show the polycrystalline wurtzite-hexagonal phase of ZnO corresponded to the standard spectrum (JCPDS cards No. 98-016-3383). Besides, no diffraction peaks from other defects (impurities) were observed, proving that the high purity of the ZnO nanocrystal phase is performed. From Figure 4, it can be noted that the fabricated ZnO thin film sample shows the sharp, strong, and dominant peak at peak position 2 q=34.3375 corresponding to the diffraction peak (002) along the c-axis of ZnO. The ZnO thin film sample resorted to growing in the orientation alongside the (002) plane to the free-surface energy (E) density of this orientation was lowest in the crystal of the ZnO [29]. The sharp, dominant, and strong peak alongside (002) diffraction peak also proven that the ZnO thin film was preferentially formed alongside the c-axis of the hexagonal-wurtzite ZnO structure with very weak diffractions peaks from other surfaces, which is confirmed that the ZnO thin film was were vertically well-aligned grow on the whole surface of glass-slide substrates. The investigated interplanar distance of synthesized ZnO thin film along (002) diffraction peak was about 2.609 Å. Also, the investigated crystal size and dislocation density of fabricated ZnO thin film alongside diffraction peak (002) was about 13.33 nm, and 5.63×10^{-5} Å, respectively.
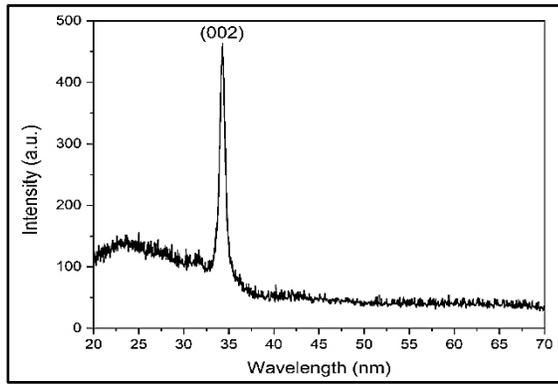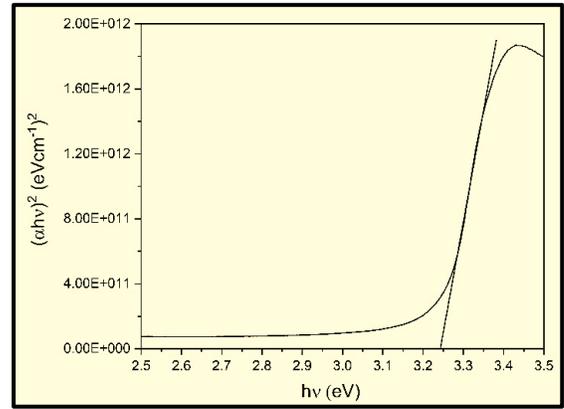
Fig. 4. XRD Pattern of Synthesized ZnO Thin Film

The optical properties of deposited ZnO thin film have studied the investigation of the optical transmissions and absorptions spectra using UV-Vis spectrometer. Figure 5 shows the transmittance of ZnO thin film with a wavelength range of (300-1000) nm. In the visible region, the fabricated ZnO thin film samples have high transmittance of more than 90% and low transmittance in the UV region. There is a sharp decrease in transmittance near the UV region at a wavelength around 383 nm. A redshift can be observed due to the change of the ZnO thin film's optical properties [30]. The shift was due to the decrement of the energy bandgap [8] and maybe assigned to the internal stress and the light scattering effects in the films caused by the random distribution of the thin film [14]. The optical absorption spectrum of the produced ZnO thin film with a wavelength range between 300 nm to 100 nm as shown in the inset of Figure 5a. The absorbance spectrum shows strong absorption i.e. high absorbance in the UV region at wavelength below 400 nm and high transparency low absorbance in the visible region, which are the characteristics of ZnO [23]. The decrease in absorbance at long wavelengths is regarded to the impurities of the ZnO thin film such as interstitial Zn atoms and oxygen vacancies, which act as donor defects [26]. Also, the investigated optical E_g of deposited ZnO thin film was about 3.24 eV, as shown in Figure 6. The obtained E_g value is in good agreement with previous studies [29].
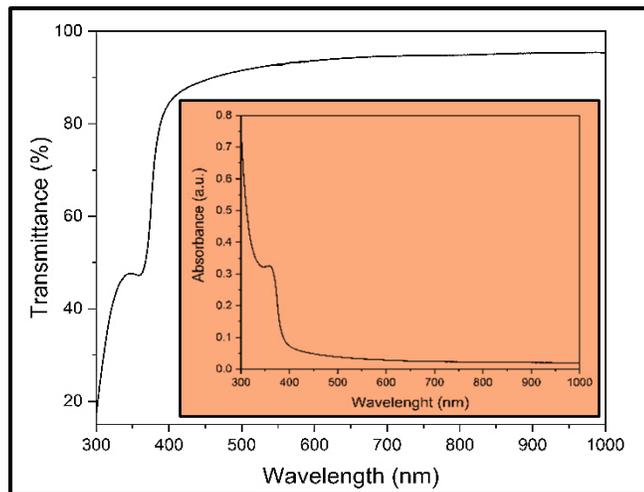

Fig. 5. Optical Transmission Spectrum of the Synthesized ZnO Thin film, the inset is Optical Absorption Spectrum of ZnO Thin Film.

Fig. 6. Tauc plot (alpha hv)^2 Versus Energy Band Gap (hv) of the ZnO Thin Film

IV. CONCLUSION

A high-quality and uniform ZnO thin film had been fabricated successfully upon the entire glass substrate via PVD technique at 37.503×10^{-3} Torr. The high purity zinc powder was heat in a chamber of PVD via molybdenum boat and oxidation at 400 °C to get ZnO thin film. The fabricated ZnO thin film was grown with a polycrystalline wurtzite-hexagonal phase of ZnO. Also, the synthesized ZnO thin film shows low absorbance and high transmittance in the visible region, and the average transmittance dropped sharply close to the UV region at 383 nm. Besides, obtained the energy band-gap (E_g) was about 3.24 eV.

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