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RESEARCH ARTICLE

Influence of Dopant Concentrations on Morphological and Optical Characteristics of Silver Doped Zinc Oxide Thin Films

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ABSTRACT - Zinc oxide (ZnO) thin films are widely used in critical applications such as solar cells, sensors, photodetectors, and conductive layers. Many efforts have been made to modify the properties of ZnO through doping so that it can be used more widely in research fields. In this work, we report silver-doped zinc oxide (Ag-ZnO) thin films by varying the Ag concentrations between 0.05 and 0.25 wt.%. The samples were prepared through the sol-gel method, followed by the spin-coating technique onto glass substrates. The work aims to investigate how different Ag concentrations affect the morphological characteristics and optical properties of the prepared Ag-ZnO thin films. The spin-coated Ag-ZnO thin film thickness was controlled at three layers to ensure the adhesion of the nanoparticles. Field Emission Scanning Electron Microscope analysis showed that as the Ag concentration increased, the particles transitioned from spherical to flake-like morphologies with smaller grain sizes. The optical energy band gap was decreased to 3.17 eV from 3.28 eV (undoped ZnO) when the concentration of Ag was the highest at 0.25 wt.%. The findings reveal that Ag doping can tailor ZnO thin films morphology and energy band gap, expanding their potential use in optoelectronic and energy devices through enhanced surface area, catalytic activity, and light absorption capabilities.

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1. INTRODUCTION

Zinc oxide (ZnO) nanoparticles is a type of metal oxide with excellent properties and is widely used in a number of commercial products and applications. ZnO is one of the transition metals that is known as metallic in nature and it has 100% internal quantum efficiency compared to other metal oxides [1]. The electrons in the outermost shell of ZnO are located in the *d*-orbital, where it is loosely bound or, in other words, is incompletely filled with electrons, so they can easily give and take electrons. In this regard, ZnO contributes to high electrical conductivity performance. Furthermore, various types of ZnO compounds can be formed due to their oxidation state of transition [2]. Recently, ZnO thin film is extensively studied due to its potential application in various fields such as gas sensors, piezoelectric transducers, ultraviolet (UV) photoconductive detectors, light-emitting diodes, laser systems, and solar cells [3-6]. ZnO thin film exhibits a bandgap of 3.40 eV and a high binding energy of roughly 60 meV. Additionally, it has a relatively wide bandgap n-semiconductor, which results in excellent oxygen efficiency, and high transparency at ambient temperature (~200 cm^2Vs^{-1}) [7].

Considerable research has focused on doping ZnO with other materials to modify its electronic, optical, and magnetic properties [8-10]. For example, doping with metals such as Ga, In, Pt, or Au has been shown to reduce grain sizes and enhance optical properties due to the presence of metallic nanoparticles. However, the high cost of noble metals like Pt and Au limits their practical use in industrial applications. Therefore, further investigation on using silver (Ag) as a doping material is crucial. Silver offers a cost-effective alternative with comparable benefits, such as enhanced optical and electronic properties. Additionally, silver's ability to reduce the bandgap energy and improve surface morphology makes it an ideal candidate for tailoring ZnO thin films for advanced applications. According to Rajendran et al., doping ZnO with Ag lowered the bandgap energy because the Ag particles were incorporated into the ZnO lattice upon doping [12]. It was also claimed that the synthesized Ag-ZnO may eliminate some of the shortcomings of undoped ZnO, including point defects such as oxygen vacancies and weak optical characteristics. Therefore, it is intriguing to further study the optical properties as well as morphological characteristics of the Ag-doped ZnO by varying the Ag concentrations. It is thought that the different Ag concentrations would affect the morphologies of the nanostructures, thereby lowering the energy band gap of the thin films. Previous study disclosed that higher concentrations of Ag as dopant would lead to ferromagnetic and semi-metallic properties as well as transitioned in the conduction type [13].

Among the various methods available to fabricate ZnO thin films, sol-gel processing stands out as a simple, cost-effective, and versatile technique. Sol-gel processing offers advantages such as low-temperature crystallization, excellent composition control, conformal deposition, and the ability to coat large surface areas [14,15]. Compared to other

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techniques, such as chemical vapor deposition or sputtering, sol-gel processing is particularly suitable for fabricating high-quality Ag-ZnO thin films in a scalable and economical manner. In this regard, the sol-gel process can regulate the nucleation and growth of ZnO crystals during the hydrolysis and condensation reactions. Meanwhile, Ag doping introduces lattice distortions, hindering the growth of ZnO grains and resulting in smaller grain sizes or altered morphologies. The use of spin-coating further ensures uniform film deposition and precise control of film thickness. Therefore, this present work investigates the influence of varying Ag concentrations (in weight percentage) on the morphological characteristics and optical properties of thin Ag-ZnO films fabricated through sol-gel processing. The thickness of the thin films was consistently set at three layers using spin-coating technique to observe the influence of the Ag concentrations and ensure adhesiveness of the thin films to the glass substrates. Field Emission Scanning Electron Microscopy (FESEM) and ultraviolet-visible spectrophotometer (UV-Vis) were utilized to examine the morphologies and optical characteristics over both undoped (pure ZnO) and doped thin films (Ag-ZnO), respectively.

2. METHODS AND MATERIAL

2.1 Materials

Zinc acetate dehydrate (Zn $(CH_2COO)_2.2H_2O$), isopropanol (C_3H_8O), Diethylamine (DEA) ($C_4H_{11}N$), silver nitrate ($AgNO_3$) and deionized water (DI). All precursors are purchased from Sigma-Aldrich and used without any purification.

2.2 Synthesis of Ag-doped ZnO Nanomaterials

Figure 1 illustrates the synthesis of Ag-doped ZnO nanomaterials using the sol-gel processing. First, undoped ZnO sol precursor was prepared by adding 3.3 g of zinc acetate dehydrate ($Zn(CH_3COO)_2.2H_2O$) into 70 mL of isopropanol and was stirred continuously for 30 minutes at room temperature until the solution became cloudy. After 10 minutes of rest, 1 mL of Diethylamine (DEA) was slowly added to the mixture under 60°C for 15 minutes until the solution became clear. The solution was stored in Schott bottle (wrap with Aluminium foil) and was placed in desiccator for aging process.

The Ag-doped ZnO was achieved by dissolution of 0.169 g of silver nitrate ($AgNO_3$) in 10 mL of deionized water which made up a 0.1 M silver solution. The mixture was stirred until clear solution was formed. Then, 0.05 %w/v of Ag-doped ZnO sol was prepared by adding the silver solution (drop by drop) into 20 mL of ZnO sol precursor and continued stirring for another 30 minutes. The steps were repeated for the 0.10, 0.20 and 0.25 %w/v Ag-doped ZnO sol precursor.

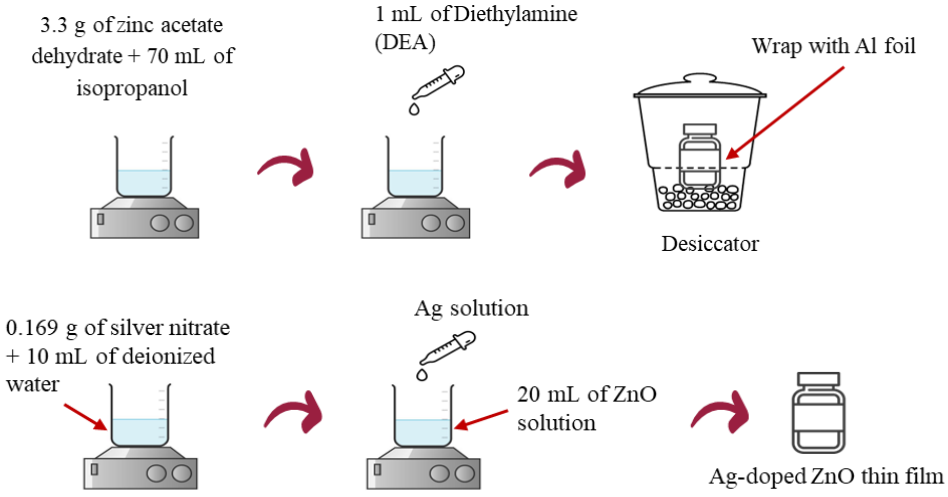


Figure 1. Schematic illustration of Ag-ZnO processing

2.3 Preparation of Ag-ZnO

Glass substrates with dimension of 2 × 2 cm were used to deposit the undoped ZnO and Ag-doped ZnO films using spin-coating technique. The Ag-doped ZnO sol was spin-coated at 3000 rpm for duration of 30 seconds. Each layer of the film was pre-treated for five minutes at 60 °C to eliminate any surplus solvent and to ensure the adherence of the nanoparticles. The thin film thickness was kept consistent at three layers. Following completion, the samples were annealed in a furnace for two hours at 300 °C. After the furnace was cooled, the samples were placed in petri dish and were ready for characterizations. The samples were labelled as undoped ZnO, 0.05%Ag-ZnO, 0.10%Ag-ZnO, 0.20%Ag-ZnO and 0.25%Ag-ZnO, respectively.

2.4 Characterizations

Surface morphology characteristics and optical absorbance of the undoped and Ag-doped ZnO films were assessed through Field Emission Scanning Electron Microscopy (FESEM) (JEOL, JSM-IT800) and UV-visible spectrophotometer (UV-Vis) (Thermo scientific model GENESYS 10S). For FESEM, the samples were coated with platinum and the voltage

was maintained at 5kV during the analysis. The UV-Vis absorption and transmittance studies were conducted over a wavelength of 200-800 nm.

3. RESULTS AND DISCUSSION

3.1 Morphological Characteristics

Figure 2 displays the morphologies of both undoped and Ag-ZnO thin films at various Ag concentrations under 60 000× magnification, while the inset shows the morphologies at 200× magnification. The undoped ZnO thin film (Figure 2(a)) has the biggest particles sizes with spherical aggregation compared to other samples. It is worth mentioning that the size particles of ZnO nanomaterials slightly decrease with Ag doping as shown in Figure 2(b). However, the small particles tend to agglomerate and aggregate when Ag concentration increased from 0.15 to 0.25% Ag as shown in Figure 2(c-e). Closer observation shows that doping with Ag would change the morphology of the ZnO nanoparticles from spherical to wrinkle flake-like microstructure. These flakes form larger aggregation and affect the compactness of the thin films. In this context, the compactness of the thin films may reduce the uniformity of the thin film, potentially creating voids or non-conductive regions. The structural change also influences the optical properties, such as light scattering or transmission. However, it is believed that in certain applications like photocatalysis, the agglomeration may enhance the catalytic performance due to high intensity of localized active sites due to the clustering of Ag particles. Similarly, for gas sensors, the non-uniform morphology might improve gas adsorption by exposing diverse surface textures. The flake-like morphology is in accordance with previous study [16-18]. Overall, the particle size of the thin films often reduced as Ag dopant concentration rose. In addition, it can be observed that the undoped film show uniform surface while the Ag-doped ZnO exhibit high compactness with the appearance of island morphology all over the surface (inset Figure 2).

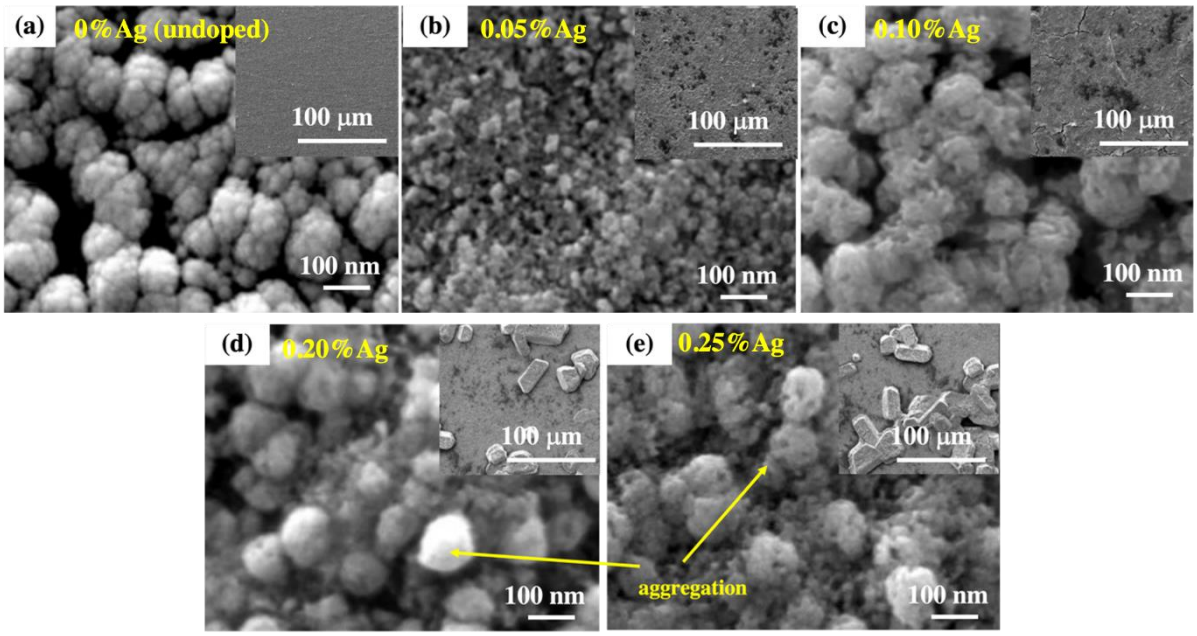


Figure 2. Surface morphologies of (a) undoped ZnO and (b – e) Ag-doped ZnO at various Ag concentrations

3.2 Optical Properties

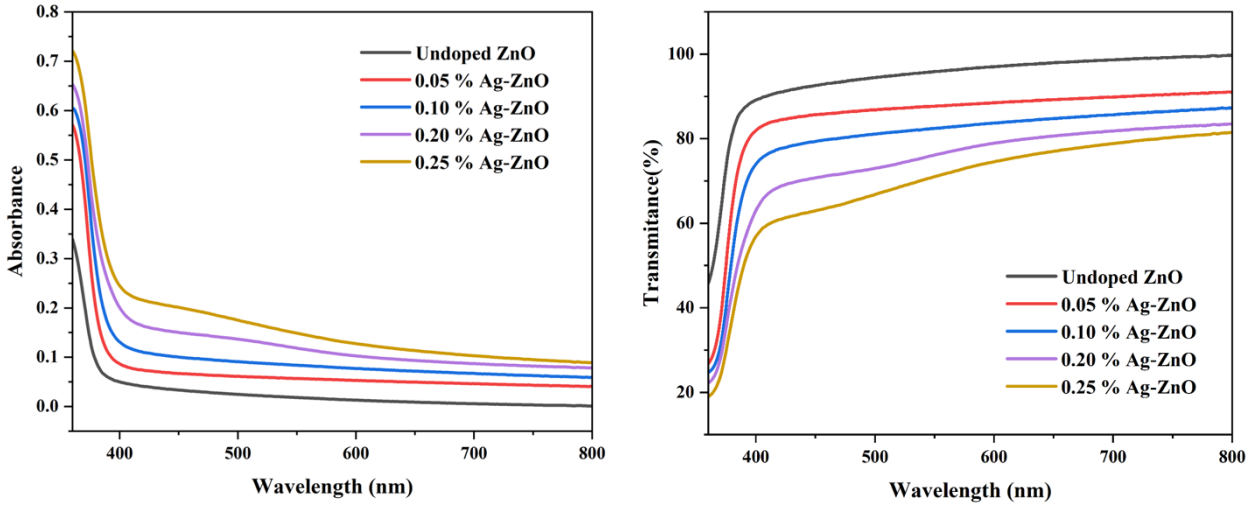
The absorption edge changes to a higher range of wavelength when the Ag concentration increases, as shown by the optical absorbance spectra displayed in Figure 3(a). The findings are aligned with the results mentioned by Kumar et al. [19]. In the meantime, the optical transmittance spectra in Figure 3(b) shows that the undoped ZnO sample exhibits an optical transmittance of more than 90% in the visible region, which indicates that the films are highly transparent. The high degree of transparency underscores the superior surface quality and the crystalline structure of the nanostructured film [20]. The spectra also distinctly displayed a change in band edge when the Ag concentration changed. It is evident that when the Ag content increases, the average transmittance marginally decreases. This effect has been linked to the scattering at grain boundaries and the absorption of visible light induced via Ag nanoparticles through surface plasmon resonance (SPR) [21,22].

Figure 4 shows the plot of hv and $(\alpha hv)^2$ for undoped and Ag-doped ZnO thin films. Tauc's relation is used to compute the optical energy bandgap [23];

$$(\alpha hv)^2 = A\,(hv - E_g)^n \quad (1)$$

where, α is absorption coefficient, hv is incident photon energy, A is a constant that depends on the electron-hole mobility that have a value between 105 cm^{-1} and 106 cm^{-1}, E_g is the optical bandgap energy and $n = 2$ for direct transition.

The undoped ZnO has predicted bandgap of 3.28 eV followed by 3.25, 3.22, 3.20 and 3.17 eV for 0.05%, 0.1%, 0.20% and 0.25%Ag-ZnO thin films, respectively. The predicted bandgap is obviously narrows as Ag concentration increases. It is hypothesized that the formation of intermediate states between the conduction and valence band of the ZnO host matrix with the addition of Ag causes the reduction the band gap of Ag-ZnO thin films. Ag functions as an acceptor material, causing the bandgap of ZnO thin film to alter and so decrease. It can be simplified that the narrowing bandgap is due to the existence of Ag impurities in the ZnO cells. Besides, decreasing in bandgap energy may be resulted from annealing process where the crystal size growth occurs during annealing, or stress is relieved as oxygen vacancies are eliminated through heat treatment in an oxygen-rich environment [24]. It was reported that the during annealing or increasing temperature, the grain size and defect also increased, thereby reducing the optical band gap due to the reduction in the lattice strain [18].



(a) (b)

Figure 3. (a) Optical absorbance and (b) Optical transmittance of undoped ZnO and Ag-doped ZnO thin films

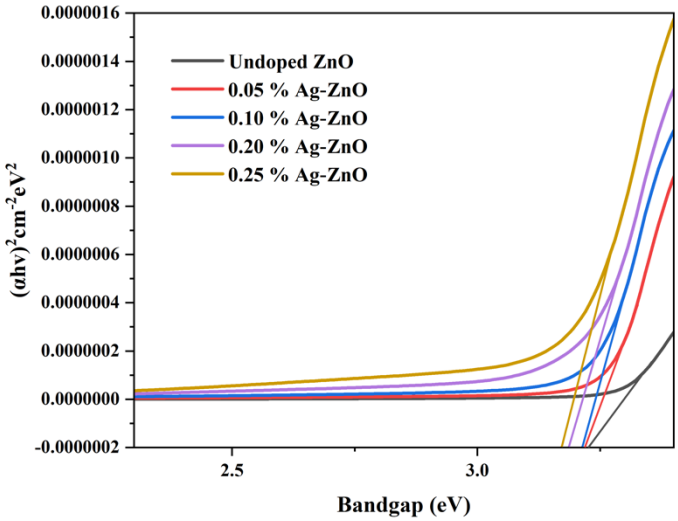


Figure 4. Energy bandgap for undoped and Ag-doped ZnO samples

4. CONCLUSION

As a conclusion, both undoped ZnO and Ag-doped ZnO thin films were successfully synthesized through sol-gel processing followed by spin coating method. The influence of Ag concentration (0.05, 0.10, 0.20, and 0.25 % w/v) on the morphological and optical characteristics were explored using FESEM and UV-Visible spectrophotometer. Examination of FESEM micrographs revealed that the films morphologies as well as the nanoparticle sizes were notably changed when the amount of Ag loading varies. Regarding the optical characteristics, it was found that as the Ag content rose, the transparency of Ag-doped ZnO thin films reduced. Additionally, the absorbtion spectra of thin films exhibited a minimal shift towards higher wavelengths, with the 0.25 % w/v Ag-doped ZnO thin film demonstrating the narrowest energy band gap (3.17 eV) among all the thin films. Overall, increasing Ag content in the thin films decrease the particle size and lower the energy band gap. The findings are inclined towards the ability of Ag loading to modify the structure

of ZnO and adeptness of the Ag-ZnO thin films in the field of transparent electrodes in solar cells, as light-emitting diodes or piezoelectric sensors.

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CONFLICT OF INTEREST

The authors declare no conflicts of interest.

AUTHORS CONTRIBUTION

N. R. Rusli: Investigation, Methodology, Writing-Original draft preparation.

N. A. S. Aziz: Writing-Reviewing and Editing.

N. F. Norapandi: Visualization, Writing- Reviewing and Editing.

N. Salim: Methodology and Validation.

N. H. A. Bakar: Supervision, Validation, Writing- Reviewing and Editing.

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