Tailoring the structural, morphological, electrical and optical characteristics of transparent and conductive ZnO/Ag-NPs thin film coatings

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Abstract. In this study, high quality ZnO/Ag-NPs thin transparent and conductive film coatings were fabricated via sol-gel process combined with spin-coating technique. Structural, surface morphology, electrical and optical properties were investigated by means of XRD, Hall effect measurements, FESEM and UV-Vis. The synthesized ZnO/Ag-NPs thin films shows a polycrystalline wurtzite structure, and the grain sizes enlarged when the annealing temperature increased. The surface morphologies of the coatings were dense, smooth and homogeneous as proved by FESEM images. The resistivity of $(5.8 \times 10^{-4} \ \Omega \cdot cm)$, the carrier concentration of $(3 \times 10^{20} \ cm^{-3})$ and the mobility of $(40 \ cm^2/V \ s)$ were obtained from the film post heated with 500 °C. Same thin film also shows the highest transmittance and energy gap of 88% and 3.71 eV respectively.

Keywords: ZnO, Transparent conductive coatings, Sol-gel, spin coating

1. Introduction

Over the past decades, optical transparency and electrical conductivity were considered inversely proportional. However, transparent and conductive materials (TCMs) have changed and wiped out this consideration through the exhibition of high optical transparency over the visible range of the light spectrum along with excellent electrical conductivity. Amongst these TCMs, transparent conductive oxides (TCOs) have been widely used in numerous optoelectronic devices including solar cells, light emitting diodes (LEDs), touch screens, displays, smart windows and sensors [1, 2]. Different materials were used as TCOs such as Indium oxide (In$_2$O$_3$) and tin-doped indium oxide known as indium tin oxide (ITO), zinc oxide (ZnO), aluminum and gallium doped ZnO (AZO, GZO), cadmium oxide (CdO) and tin oxide (SnO$_2$) [3, 4]. ZnO-based thin TCOs coatings have been widely used recently owing to its non-toxic, high stability and good optoelectronic properties. The TCOs based thin film coatings were produced so far via RF and DC sputtering, pulsed laser deposition, thermal evaporation, and sol-gel processes [5, 6]. The sol-gel is cheap, able to control the doping concentration, performed at low temperature and short time and produced coatings with preferred shape and surface area [7, 8]. ZnO can be doped with different elements including some transition metals such as aluminum (Al), silver (Ag), gallium (Ga), copper (Cu), indium (In), Titanium (Ti) etc. [9-11]. Combining silver nanoparticles (Ag-NPs) which have a reasonably good electrical conductivity and high optical transparency with ZnO has not been widely overlooked and discussed.
In this study, highly transparent and conductive system of ZnO/Ag-NPs was deposited on glass substrates by sol-gel spin-coating method. The thicknesses and the concentrations of both ZnO and Ag-NPs coatings were kept consistent throughout the sample fabrication process and the prepared thin films were post annealed at different annealing temperatures (300, 400 and 500) °C. Such kinds of bilayer systems have not been extensively studied by researchers. The main goal of this investigation is to point out the role of Ag-NPs and annealing temperature on the structural surface topography, electrical and optical characteristics of ZnO coatings.

2. Methodology

2.1. Materials and methods

ZnO and Ag-NPs sols have been prepared using Zinc acetate dehydrate (Zn(CH₃COO).2H₂O), purity 99.99%, Silver nitrate (AgNO₃, 99.5%), sodium borohydride (NaBH₄, 99.6%), 2-methoxy ethanol (C₃H₆O₂), purity 98%, mono ethanolamine (C₂H₇NO), purity 98% and polyvinylpyrrolidone (PVP, M = 40000g/mol). All the aforementioned chemicals were used without any purification.

A ZnO solution with 0.2 M was prepared by dissolving the appropriate amount of zinc acetate in 2-methoxy ethanol and stirring for 2 hours at 60 °C on a magnetic stirrer. The ethanolamine with a molar ratio of 1:1 was added to the resultant solution and stirred for another 2 hours at 60 °C.

The Ag nanoparticle solution was prepared with a concentration of 0.2 M. The required amount of silver nitrate was dissolved in 10 ml of de-ionized (DI) water. The concentration of NaBH₄ was kept consistent at 0.2 M in this work. In order to prepare the NaBH₄ solution, an adequate weight of sodium borohydride was dissolved and vigorously stirred in 50 ml DI water, and the obtained solution was chilled in an ice bath prior to the addition of AgNO₃ sol. The resultant mix was further stirred until a yellow solution was obtained.

The chemical reaction and reduction of AgNO₃ could be characterized by the following reactions [12, 13]

\[
2 \text{AgNO}_3 + 2 \text{NaBH}_4 \rightarrow 2 \text{Ag} + \text{H}_2 + \text{B}_2\text{H}_6 + 2 \text{NaNO}_3 \quad (1)
\]

\[
\text{Ag}^+ + e^- \rightarrow \text{Ag} \quad (3)
\]

The ZnO/Ag-NPs thin film coatings were fabricated by depositing 50±5 nm Ag nanoparticles thin films onto 25×25 mm² dimensions glass substrates followed by pre-heat treatment at 150 °C for 1 hour. Then, 150±10 nm of ZnO thin film was deposited onto Ag-NPs thin films followed by pre-heating the resultant ZnO/Ag-NPs thin films at 150 °C for 1 hour. The spin-coating process for synthesizing ZnO/Ag-NPs thin films was performed at 3000 rpm for 30 seconds, and the resultant coatings were heat treated in air atmosphere at (300, 400 and 500) °C.

2.2. Characterization techniques

The crystallographic features of the ZnO/Ag-NPs films were characterized via (XRD) examination using a Siemens diffractometer with Cu-Kα source (λ=0.154nm). The surface topography was imaged using JEOL JSM-6301 (FESEM). The optical characteristics were carried out using UV-VIS spectrometer. The electrical properties were performed using a Dasol Eng. FPP-HS8 4-point probe, while the ECOPIA HMS-2000 instrument was used for Hall-effect measurements.

Scherrer relation was used to estimate the mean particle size of the synthesized ZnO/Ag-NPs thin films [14].

\[
D = \frac{0.89\lambda}{β\cosθ} \quad (4)
\]

where λ is the wavelength of X-ray beam, β is the line width at FWHM and θ is Bragg’s diffraction angle.

The electrical resistivity (ρ) and conductivity (σ) are given by the following relations [15, 16]:

\[
ρ = \frac{π}{ln(2)} t \left(\frac{V}{I}\right) \quad (5)
\]

\[
σ = N_e \times μ \times e \quad (6)
\]
where $t$ is the film thickness, $V$ is the voltage across the inner two probes and $I$ is the current passed through the outer two probes, $N_e$ is the carrier concentration, $\mu$ is the carrier mobility and $e$ is the electron charge.

The free carrier mobility $\mu$ can be defined as:

$$\mu = \frac{e\tau}{m_e}$$  \hspace{2cm} (7)

where $m_e$ is the effective electron mass in the conduction band and $\tau$ is the average collision time of electrons.

The absorption coefficient ($\alpha$) of the thin films can be calculated from the following equation [17]:

$$\alpha = \frac{1}{t} \ln \left( \frac{1}{T} \right)$$  \hspace{2cm} (8)

where $t$ is the film thickness and $T$ is the optical transmittance.

The transmittance and the absorption can be computed from the following equations [18]:

$$T = A \times \exp \left( -\frac{4\pi k}{\lambda} t \right) \sim \exp(-\alpha t)$$  \hspace{2cm} (9)

$$A = \frac{16 n_o n_1 (n^2 + k^2)}{(n^2 + k^2)^2 + (n_o + n)^2 (n_o - n)^2 + k^2}$$  \hspace{2cm} (10)

where $n_o$, $n$ and $n_1$ are the refractive indices of air, film and substrate, respectively and $k$ is the extinction coefficient.

The band gap energies ($E_g$) for the prepared thin films were estimated using the formula [18]:

$$(\alpha h\nu)^2 = A(h\nu-E_g)$$  \hspace{2cm} (11)

where $\alpha$ is the absorption coefficient, $h\nu$ photon energy, $A$ constant represents the proportionality coefficient, $E_g$ the energy band gap and $n = 1/2$ for allowed direct transitions.

3. Results and discussions

3.1. Descriptions of Ag-NPs colloidal solution

The mechanism of reduction Ag ions by NaBH$_4$ to form Ag nanoparticles follows three main steps. Once the solutions mixed, the first step starts, and the tiny particles of 3 nm were grown. As the reaction continues (the second step), the Ag particles further grow within a period of (20 – 60 min) reaching (8 – 20 nm). In the final step, all the NaBH$_4$ is used. Accordingly, the stabilizing BH$_4^-$ is consumed, and the solution changed from reducing state to the oxidizing state [19]. Both the modifications of the surface potential of Ag particles and the adsorption of BH$_4^-$ promote the agglomeration of Ag-NPs.

The distinctive colours of Ag-NPs solution are mainly assigned to the plasmon absorbance, especially when the incident light promotes the vibrations of the electrons at Ag-NPs surfaces subsequently, the light is absorbed [20, 21]. From figure 1, the absorption peak of Ag-NPs solution was located at 405 nm. It has been evident that the shape and the position of the absorption peak of metal-NPs depend on the particle size and the dielectric medium [22]. Also, Van Hyning et al. stated that the maximum of the plasmon absorption peak for Ag-NPs solution at 405 nm wavelength is attributed to the formation of a grain size of (10 – 14) nm [19].

![Figure 1. Absorption spectrum of prepared Ag-NPs solution](image-url)
3.2. Crystalline structures

Figure 2 shows the XRD outlines of ZnO/Ag-NPs thin films post annealed at different temperatures. From figure 2, synthesized films exhibited polycrystalline feature with sharp and intense peaks correspond to the wurtzite structure of ZnO as expected and $P6_{3}mc$ space group (JCPDS card 070-8070) [23]. The peaks of ZnO/Ag-NPs coatings observed at $2\theta$ values of $31^\circ$, $34^\circ$, $36^\circ$, $47^\circ$, $56^\circ$ and $63^\circ$ are linked to (100), (002), (101), (102), (110) and (103) reflection orientations respectively. This may be attributed to the early coalescence of the Ag-NPs coating that facilitates the growing of high quality top ZnO layer, and reduces the effect of the thermal expansion mismatch between the glass and the ZnO film. With increasing the calcination temperature, the polycrystalline structures for all the synthesized thin films were improved, and the film treated with $500^\circ$C shows the most intense peak as seen in figure 2. This is because at high temperature the ZnO particles supplied with a sufficient energy to accumulate at the preferred (002) orientation. Also, high annealing temperature assists the diffusion and the accumulation of Ag-NPs within the ZnO matrix by increasing the thermal energies of these particles and/or substituting of the Zn atoms in their sites by Ag atoms. It has been reported by Cao and co-workers [24] that the energetic particles in a crystalline structure tend to gathering and accumulating along the preferred orientation plane lead to improve the crystalline quality.

Scherrer relation (Eq. 4) was used to estimate the mean particle size of the synthesized ZnO/Ag-NPs thin films. The grain size of ZnO/Ag-NPs coatings is enlarged with increasing the calcination temperature and the highest value of $D$ was found to be 45 nm for the film annealed at $500^\circ$C due to enhance the substitution of Zn by Ag ions, and the agglomeration of the Ag particles in the grain boundaries of ZnO matrix which lead to decrease the density of the grain boundaries and hence improve the crystalline quality. Liu and co-authors [25] have been reported the same tendency of enlarging the crystallite size of both Ag-NPs and ZnO thin film and they stated that the crystalline structure of ZnO thin film did not changed with introducing Ag-NPs to the film material.

3.3. Surface morphology
Figure 3 shows the FESEM images of annealed ZnO/Ag-NPs thin films. All the fabricated coatings exhibited uniform, smooth, dense and homogenous surfaces confirming the growing of a crystalline feature of ZnO. This could be attributed to the formation of continuous Ag-NPs coating underneath the ZnO coating which assists the growing of homogenous and free pinholes surface morphology for ZnO coating. Also, high annealing temperature results in improving the surface morphology along with increasing the grain sizes of the fabricated ZnO-based thin films.

![FESEM images for post annealed Ag-NPs thin films](image)

**Figure 3.** FESEM images for post annealed Ag-NPs thin films

### 3.4. Electrical properties

Figure 4 (a and b) displays the variations of the resistivity, conductivity, carrier concentration and mobility of annealed ZnO/Ag-NPs thin films with annealing temperature. In general, the average resistivity of the ZnO/Ag-NPs thin films is low enough comparable to those for ITO-based thin films in our previous study [26]. This confirms that ZnO-based thin transparent and conductive coatings can be good choice to substitute the expensive ITO material. With increasing annealing temperature from 300 °C to 500 °C, the resistivity is reduced from $7.8 \times 10^{-4} \Omega \cdot \text{cm}$ to $5.8 \times 10^{-4} \Omega \cdot \text{cm}$ while the conductivity is improved from 1282 S.cm$^{-1}$ to 1724 S.cm$^{-1}$. Moreover, the carrier concentration and the mobility of the synthesized ZnO/Ag-NPs thin films are also improved and the highest values of the carrier concentration (~ $3 \times 10^{20}$ cm$^{-3}$) and mobility (~ 40 cm$^2$/Vs) were obtained for the film annealed at 500 °C. This could be assigned to the role of annealing temperature that assists the diffusion of Ag atoms through ZnO matrix either to substitute Zn atoms on their sites (as discussed previously) or to occupy random sites and growing as coalescences of Ag particles and hence forming effective conducting paths for the charge carriers. It has been reported that the free electrons prefer to transport through these conducting paths rather than ZnO matrix, and these paths also enhance the carrier mobility of the thin film [27]. Furthermore, annealing temperature results in enhancing the crystalline structure and enlarging the grain size of fabricated thin films as proved in the XRD analysis. Accordingly, the density of grain boundaries reduced and the chained electrons liberated thus the number of the charge carriers in the thin film matrix increased.
3.5. Optical properties

Figure 5 (a and b) displays the transmittance spectra and the variation of the optical band gap energy of ZnO/Ag-NPs thin films. The optical transmittance of all the thin films strongly depends on the annealing temperature and it is increased from 85% to 88% after increasing the annealing temperature from 300 °C to 500°C. This can be attributed to the high uniformity of both the ZnO top layer and the Ag-NPs bottom layer, as well as the low density of the scattering centres along with low absorption of incident photons. In addition, increasing annealing temperature enhances growing of continuous thin film coatings. Despite the obtained optical transparency of ZnO/Ag-NPs thin films in this investigation is poorer than that obtained for ITO-based thin films in our previous study [28], it stills considered adequate for optoelectronic devices.

The calculated energy band gaps of annealed ZnO/Ag-NPs thin films are presented in figure 5b. The results show that the ZnO/Ag-NPs thin films have high energy band gap values indicating a band gap broadening takes place. This is an expected behaviour due to higher optical transmittance of the ZnO/Ag-NPs thin films. Also, widening the energy band gap could be linked to the enhancement of the crystallographic features of ZnO/Ag-NPs films and enlarging the grain size along with increasing annealing temperature onto deposited thin films. The $E_g$ for annealed ZnO/Ag-NPs thin film was increased from 3.68 eV to 3.71 eV when the annealing temperature increased from 300 °C to 500°C. This could be attributed to improving the crystalline quality through enlarging the crystallite size and
reducing the density of grain boundaries in the thin film matrix owing to increasing the annealing temperature. [28].

![Graph](image)

**Figure 5.** a- Transmittance and b- energy gaps of annealed ZnO/Ag-NPs thin

4. Conclusions
ZnO/Ag-NPs thin transparent conducting oxide coatings were successfully fabricated via a sol-gel spin-coating technique. The effects of annealing temperature on the structural, surface morphology, electrical and optical properties of these thin films were investigated. Combining Ag-NPs layer underneath ZnO layer did not affect the ZnO structure. The grain of these coatings is enlarged with further annealing, and the highest value was obtained for the film annealed at 500 °C. FESEM images show that all the thin films display uniform, smooth, dense and homogenous surface with a grain feature indicating a polycrystalline structure of ZnO phases. The electrical resistivity of the prepared thin films was dropped along with increasing annealing temperature achieving the lowest values of $5.8 \times 10^{-4}$ Ω.cm. The maximum optical transparency in the visible region and the largest $E_g$ were 88% and 3.71 eV respectively.
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