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The effect of different annealing conditions in undoped and Ag-doped ZnO thin films grown by SILAR method

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Abstract

Undoped, %3 and %5 Silver (Ag) doped zinc oxide (ZnO) thin films have been grown on glass substrates by simple and economic successive ionic layer absorption and reaction method (SILAR). All grown films were annealed vacuum and air to investigate to effective annealing at 573 K for 30 minutes. Also, the prepared samples were analyzed by Energy-Dispersive-X-Ray-Fluorescence (EDXRF) spectroscopy. Absorbance measurements showed that the optical bandgaps of all thin films were wide and generally decrease with annealing. Optical transmittance spectra of ZnO and %3 and %5 doped ZnO thin films showed good transmissions. The thickness of the films was measured by the gravimetric weight difference method using sensitive microbalance.

Keywords: Anneal effect, SILAR, Ag-doped ZnO, absorbance, optical transmittance

1. *Introduction*

ZnO is one of the most important material having direct bandgap and high excitation binding energy of 60 meV at room temperature (RT) (COŞKUN *et al.* 2009; SINGH *et al.* 2015), transparency in visible range of solar spectrum (JAMBURE *et al.* 2014). ZnO also has been widely preferred for a photocatalyst, owing to its high activity, low cost and friendly environment (BECHAMBI *et al.* 2015). The most powerful technique to adapt the optical and electrical properties of semiconductor optoelectronic devices directly applicable in is doping (SINGH *et al.* 2015). Bandgap of ZnO can be changed depending on the growth conditions and dopant. Some dopant elements can be easily doped ZnO semiconductor and bandwidth can be controlled so ZnO is a promising photonic material for optoelectronic device technology by its feature (GÜNEY and ERTARĞIN 2015).

ZnO can grow different chemical methods such as SILAR (GÜNEY and ERTARĞIN 2015), Spray Pyrolysis (SP) (OLVERA *et al.* 2002), Chemical Bath Deposition (CBD) (SHINDE *et al.* 2005), Electerodeposition (ECD) COŞKUN *et al.* 2009), etc. ZnO thin films of compound semiconductors can be deposited alternately by means of the dipping substrate into the aqueous solutions containing ions for each component via SILAR method (GÜNEY and ERTARĞIN 2015). The growth of thin films during the SILAR method occurs solely heterogeneously on the solid–solution interface due to the intermediate rinsing step between the cation and anion immersions. Therefore, the thickness of the film can easily be controlled by the number of growth cycles and time (GAO *et al.* 2004; YILDIRIM *et al.* 2009). Doping can be done easily during the SILAR method. In this way, this method becomes more useful in some semiconductor growth. One of the most important advantages of this method does not require high temperature and vacuum environment but also semiconductors method which requires competitors to be able to produce that situation.

The aim of the present work is to investigate the effect of different annealing conditions on optical properties of undoped, 3% and 5% Ag-doped ZnO thin films. To this end, first undoped and Ag-doped ZnO thin films prepared by SILAR methods. Afterward various properties of samples were analyzed at each annealing temperature.

2. *Experimental*

ZnO thin films were grown on glass substrate by the SILAR method. Firstly, the substrate was cleaned subsequent 5 min. trichloroethylene 5 min. acetone and 5 min. methanol. Zinc cation procedures were made to obtained Zinc ammonium complex solution ($[Zn(NH_3)_4]^{2+}$). This procedure is 0.1 M $Zn(NO_3)_2$ and concentrated 29% ammonia NH_4OH (1:10). For Ag dopant different molar, $AgNO_3$ was added in the cation solution. This procedure is a two-step process involving subsequent immersion of cleaned substrate in cationic and near boiling DI water.

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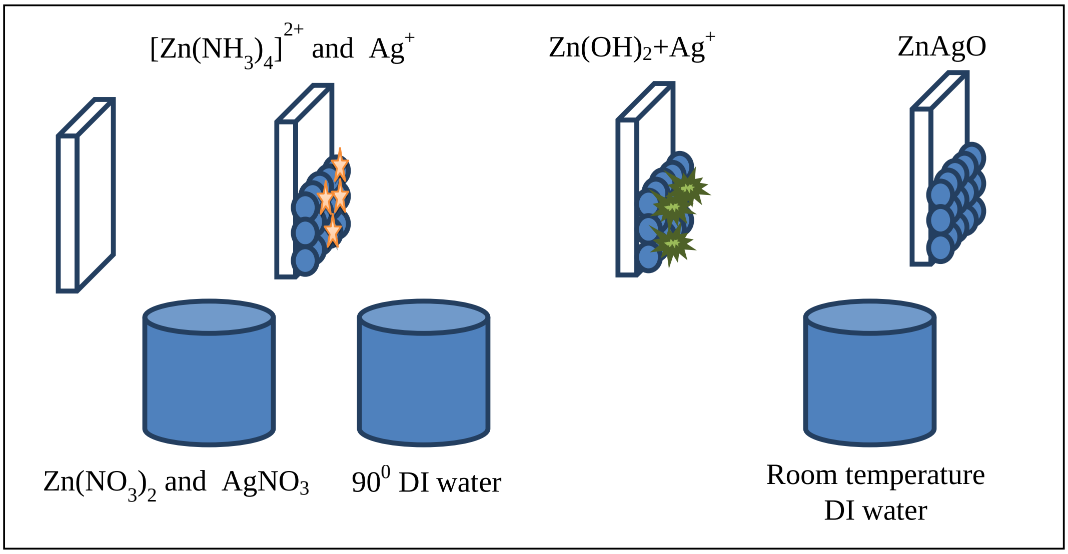

Figure 1. Schematic representation of ZnAgO growth by SILAR method

Growth procedure;

a. The cleaned glass substrate was immersed in the cation solution for 20 s at room temperature so that zinc complex and doping Ag were adsorbed on the substrate surface.

b. The substrate was immersed in 95°C DI hot water for 20 s to form the ZnO film.

c. The substrate was hanged on in the air to drying for 20 s.

d. The substrate was immersed at room temperature DI water for 20 s to form the ZnO film.

40 deposition cycles were made. Fig.1. shown schematic representation of ZnAgO by SILAR method.

All films were annealed at 573 K in vacuum and air for 30 minutes. The optical properties were investigated using UV-1800 spectrophotometer. The EDXRF analyses have been recorded using a Skyray EDX P730. Thickness of the films was measured by weight difference method using sensitive microbalance.

3. *Result and Discussion*

The mechanism of ZnO films formation by SILAR method can be explained as follows (SHINDE *et al.* 2007; GÜNEY and ERTARĞIN 2015).

$Zn(NO_3)_2+2NH_4OH \rightarrow Zn(OH)_{2(s)}+2NH_4^++2NO_3^-$ (1)

$Zn(OH)_2(s)+4NH_4 \rightarrow [Zn(NH_3)_4]_2++2H_2O+2H^+$ (2)

$[Zn(NH_3)_4]_2++H_2O \rightarrow Zn^{2+}+NH^{4+}+OH^-$ (3)

$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2$ (4)

$Zn(OH)_2 \rightarrow ZnO_{(s)} + H_2O$ (5)

When substrate glass is immersed in formed this solution, these zinc complex ions and Ag ions get

According to Pathan and Lokhande, these forces may be cohesive forces or Vander Waals forces or chemical attractive forces (PATHAN and LOKHANDE 2014).

All samples to determine the effect of annealing were annealed at 573 K for 30 minutes in vacuum and air atmosphere. To get additional information about the effect of annealing on thin films, we have calculated bandgap energy from the optical absorption of the grown structures before and after annealing.

The representative EDXRF patterns of ZnO and 3% and 5% doped ZnO thin films growth by SILAR are shown in Figure 2. The oxygen peaks aren't shown because measurable elements are from sulfur to uranium of using EDXRF.

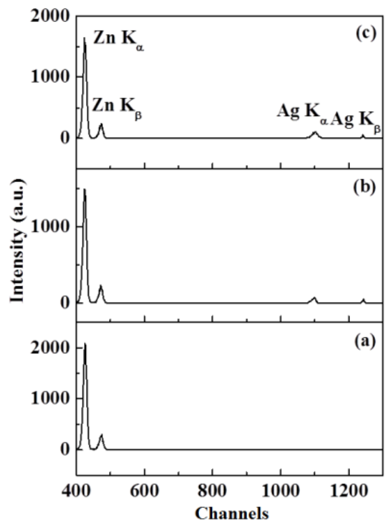

Figure 2. EDXRF spectra of ZnO a) undoped ZnO b) %3 Ag-doped ZnO c) %5 Ag-doped ZnO

According to UV-vis absorption spectra collected of ZnO films absorption spectra measurements were converted from the absorption coefficient for observing variation optical bandgap by the following equation,

$$(\alpha h\nu) = B(h\nu - E_g)^{1/2} \quad (6)$$

where α is absorption coefficient, E_g is optical bandgap and *B* is constant (GOMEZ *et al.* 2005).

Figure 3 shows absorbance and optical transmittance spectra of ZnO and 3% and 5% doped ZnO thin films growth by SILAR and after being annealed once at 573 K in vacuum and air. All films exhibit good transmission (generally higher than 15%) in the studied range which means the antireflection character of the films in the visible region (TORTOSA *et al.* 2007).

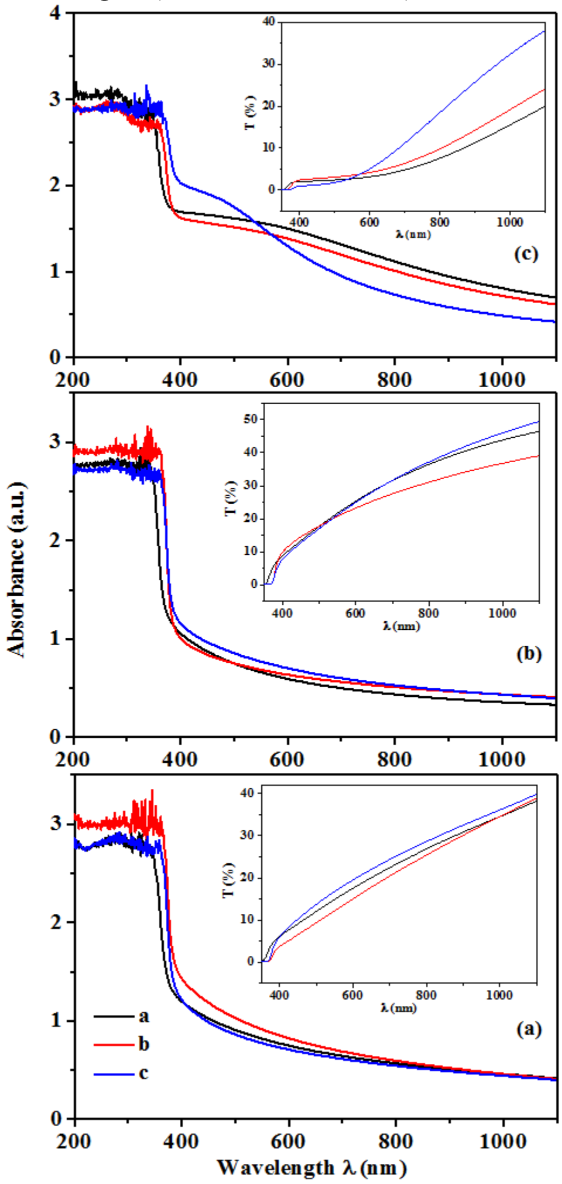

Figure 3. Absorbance and optical transmittance spectra of ZnO (a-non annealed, b-573 K under vacuum annealed, c-573 K under air annealed) a) undoped ZnO b) 3% Ag-doped ZnO c) 5% Ag-doped ZnO

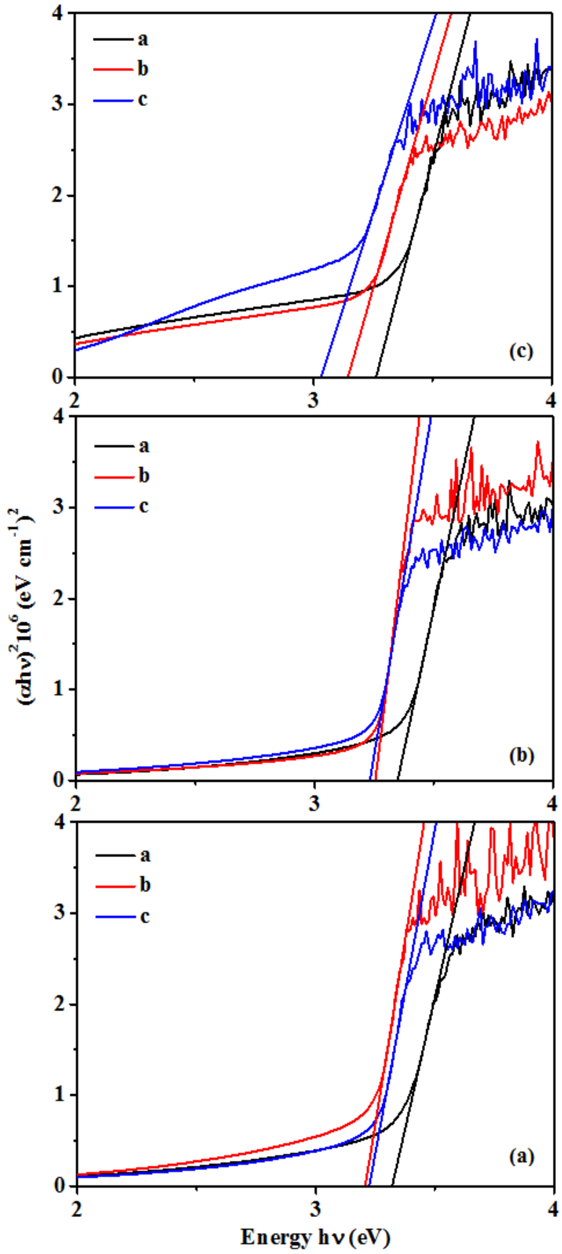

Figure 4. (αhν)2 versus energy (hν) of ZnO (a-non annealed, b-573 K under vacuum annealed, c-573 K under air annealed) a) undoped ZnO b) 3% Ag-doped ZnO c) 5% Ag-doped ZnO

Figure 4 shown via calculated equation 6 the variation of $(\alpha h\nu)^2$ versus energy (hν). Table 1 shows varieties of band-gap of all samples. Figure 4 and Table 1 show that all films bandgaps decreased with annealing. Bandgap is higher unannealed to both in vacuum and air annealed samples. This bandgaps decreases might have resulted from the annealing where oxygen loss from the surface is impossible so that the material may become relatively more O-rich at the annealing temperatures and has lower bandgap energy after annealing (COŞKUN *et al.* 2009).

Table 1. Bandgap values of samples a) non-annealed, b) under vacuum annealed and c) under air annealed of undoped ZnO, 3% Ag-doped ZnO and 5% Ag-doped ZnO.

Sample (ZnO)	a (eV)	b (eV)	c (eV)
undoped	3.32	3.20	3.23
%3 Ag-doped	3.35	3.25	3.23
%5 Ag-doped	3.27	3.17	3.05

Thickness of ZnO and doped 3% and 5% Ag-ZnO films was calculated by the gravimetric weight difference method in terms of deposited weight of a copper iodide film on the glass substrate, per unit area (g/cm^2). Using formula for the thickness was calculated,

$$T = \frac{M}{\rho A} \tag{7}$$

where 'T' is film thickness, 'M' is mass of the film material in gm, 'A' is area of the film in cm^2 and ρ is density of the film material ($\rho = 5.61$ g/cm^3) (BULAKHE *et al.* 2013). Table 2 shows that all samples' thickness.

Table 2. Thickness values for sample undoped ZnO, 3% Ag-doped ZnO and 5% Ag-doped ZnO.

Sample (ZnO)	Thickness (μm)
undoped	0.72
%3 Ag-doped	0.30
%5 Ag-doped	0.45

These results show that the thickest sample is undoped ZnO, but the thinnest sample is 3% Ag-doped ZnO so Ag dopant effect to the growth of samples by SILAR method.

4. Conclusion

In summary, we have presented a simple SILAR method for the growth of unannealed, 3% and 5% doped ZnO thin films successfully growth on to glass substrates by SILAR. Studies on Ag-doped ZnO semiconductor has not been observed in the literature by SILAR method. Thus, this study is the first in the literature.

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