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Effective annealing of ZnO thin films grown by three different SILAR processes

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Abstract

In the present work, zinc oxide (ZnO) thin films have been grown three different cation solution on glass substrates by a simple and economic successive ionic layer absorption and reaction method (SILAR). One of each grown different solution films was annealed to investigate to effective annealing at 300 °C for 30 minutes. Adsorption measurements showed that the optical band-gaps of all ZnO thin films were wide and were about 3.08-3.31 eV. All films' band gap increased with annealing. Energy-Dispersive-X-Ray-Fluorescence (EDXRF) spectroscopy showed Zn in structures. Wettability of all films was analyzed using a CCD camera. It was found that without any surface modification all films show hydrophobic behavior. Thickness of the films was measured by the gravimetric weight difference method using sensitive microbalance. Thickness of the films increased with annealing. Conductivity of all films was measured by hot probe method and each film shown n-type conductivity.

Keywords: ZnO, SILAR, annealing, hydrophobic

1. Introduction

ZnO is a very important material in manufacturing thin film solar cells with hexagonal wurtzite structure and wide and direct band gap energy of 3.4 eV at room temperature (RT) (COSKUN *et al*. 2009), transparency in visible range of solar spectrum (JAMBURE *et al*. 2014). Through its typical properties it has been used in multiple applications (VARGAS-HERNANDEZ *et al*. 2008). ZnO is a promising photonic material for optoelectronic device technology by its feature. Band gap of ZnO can be changed depending on the growth conditions. In this way, ZnO becomes more useful in optoelectronic applications.

ZnO can grow different chemical methods such as SILAR (YILDIRIM and ATES 2010), Spray Pyrolysis (SP) (DE LA OLVERA *et al*. 2002), Chemical Bath Deposition (CBD) (SHINDE *et al*. 2005), Electrodeposition (COSKUN *et al*. 2009), etc. Thin films of compound semiconductors can be deposited alternately by means of the dipping substrate into the aqueous solutions of containing ions for each component via SILAR method (NICOLAU 1985). 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 used (GAO *et al*. 2004; YILDIRIM *et al*. 2009).

In this work the effect of annealing and different solutions optical properties of grown ZnO transparent films prepared by SILAR deposition method is investigated.

2. Experimental

On glass substrate ZnO thin films were grown there different solution procedures by the SILAR method. Firstly, substrate was cleaned subsequent 5 min. trichloroethyle 5 min. acetone and 5 min. methanol. Three different zinc cation procedures were made to obtained Zinc ammonium complex solution ($[Zn(NH_3)_4]^{2+}$). These procedures are

- 0.1 M $ZnCl_2$ and concentrated 25-28% NH_3 (1:10)
- 0.1 M $ZnSO_4$ and concentrated 29% ammonia NH_4OH (1:10)
- 0.1 M $ZnNO_4$ and concentrated 29% ammonia NH_4OH (1:10)

Each procedure is a two steps process involving subsequent immersion of cleaned substrate in cationic and near boiling DI water.

Growth procedure 1:

a. The cleaned glass substrate was immersed in the zinc complex ($[Zn(NH_3)_4]^{2+}$) solution for 14 s at room temperature so that zinc complex was adsorbed on the substrate surface.

b. The substrate was immersed in 95°C DI hot water for 6 s to form the ZnO film.

c. The substrate was hanged on in the air to drying for 50 s. 60 deposition cycles were made.

Growth procedure 2:

a. The cleaned glass substrate was immersed in the zinc complex ($[Zn(NH_3)_4]^{2+}$) solution for 2 s at room

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temperature so that zinc complex was adsorbed on the substrate surface.

b. The substrate was immersed in 95°C DI hot water for 2 s to form the ZnO film. 100 deposition cycles were made.

Growth procedure 3:

a. The cleaned glass substrate was immersed in the zinc complex ($[Zn(NH_3)_4]^{2+}$) solution for 2 s at room temperature so that zinc complex was adsorbed on the substrate surface.

b. The substrates in 95°C DI hot water for 2 s to form the ZnO film. 160 deposition cycles were made.

All films were annealed at 300°C for 30 minutes. The optical properties were investigated using Shimadzu UV-1800 spectrophotometer. The EDXRF analyses have been recorded using a Skyray EDX P730. Wettability of all films was analyzed using a CCD camera. Thickness of the films was measured by weight difference method using sensitive microbalance.

3. Result and Discussion

The mechanism of three different ZnO films formation by SILAR method can be explained as follows.

- $ZnCl_2$

  $2ZnCl_2 + 4NH_3 \rightarrow 2[Zn(NH_3)_4]^{2+} + 2Cl^-$ (1)

- $Zn(NO_3)_2$

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

  $Zn(OH)_2(s) + 4NH_4^+ \rightarrow [Zn(NH_3)_4]^{2+} + 2H_2O + 2H^+$ (SHINDE *et al*. 2007) (3)

- $ZnSO_4$

  $ZnSO_4 + 2NH_4OH \rightarrow Zn(OH)_2 + 2NH_4 + SO_4^{2-}$ (4)

  $Zn(OH)_2 + 4NH_4 \rightarrow [Zn(NH_3)_4]^{2+} + 2H_2O + 2H^+$ (JIMÉNEZ-GARCÍA *et al*. 2014) (5)

In these reactions, when aqueous ammonia and ammonium hydroxide solution at 1:10 ratio was added to the zinc chloride, zinc sulfate and zinc nitrate solutions, the ionic product of zinc ammonium complex solution ($[Zn(NH_3)_4]^{2+}$). The detailed chemical reactions of $[Zn(NH_3)_4]^{2+}$ are given as follows:

$[Zn(NH_3)_4]^{2+} + H_2O \rightarrow Zn^{2+} + NH^{4+} + OH^-$ (6)

$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2$ (7)

$Zn(OH)_2 \rightarrow ZnO(s) + H_2O$ (SURESH KUMAR *et al*. 2008) (8)

When substrate is immersed in formed these solutions, these zinc complex ions get adsorbed surface of the substrate due to attractive force between ions in the solution and surface of the substrate. These forces may be cohesive forces or Van der Waals forces or chemical attractive forces (PATHAN and LOKHANDE 2004).

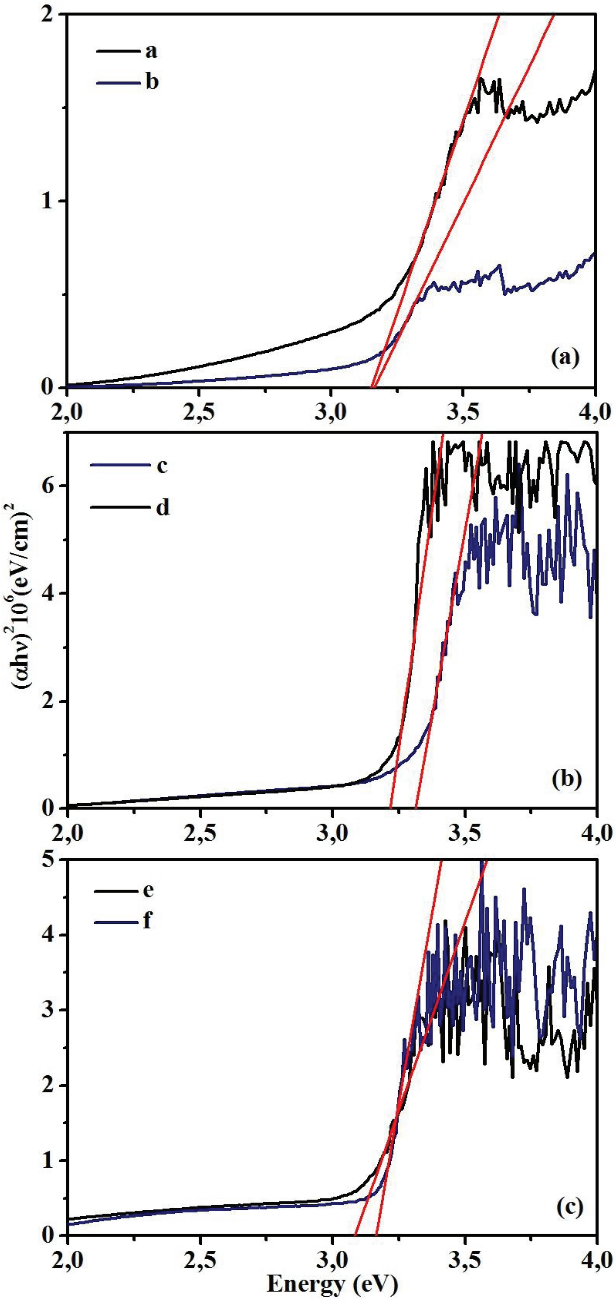

Fig. 1 (αhν)2 versus energy of respectively non-annealed and annealed prepared different solution ZnO
a) a non-annealed and b annealed with $ZnCl_2$
b) c non-annealed and d annealed with $Zn(NO_3)_2$
c) e non-annealed and f annealed with $ZnSO_4$

All samples to determine the effect of annealing were annealed at 200 degrees for 30 minutes. Thus prepared with different solutions ZnO semiconductor was observed after annealing for the change.

In order to get additional information about the effect of this particular heat treatment on the SILAR-grown ZnO thin films, we have calculated from the optical absorption of the grown structures before and after annealing.

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

$$(\alpha h\nu) = B(h\nu - E_g)^{1/2} \tag{9}$$

where α is absorption coefficient, E_g is optical band gap and B is constant (GOMEZ *et al*. 2005). Fig. 1 shows the variation of $(\alpha h\nu)^2$ versus energy. Table 1 shows varieties of band-gap of all samples. Fig.1 and Table 1. show that all films band gaps increased with annealing.

Table 1. Band gap values for ZnO thin films. (a non-annealed and b annealed with $ZnCl_2$, c non-annealed and d annealed with $Zn(NO_3)_2$, e non-annealed and f annealed with $ZnSO_4$)

Band-gap energies of same sample non-annealed and annealed (eV)			
Sample	a-b	c-d	e-f
Non-annealed	3.15	3.22	3.08
Annealed	3.17	3.31	3.16

The representative EDXRF patterns of ZnO thin films are shown in Fig. 2. The oxygen peaks isn't show because measurable elements are from sulfur to uranium of using EDXRF.

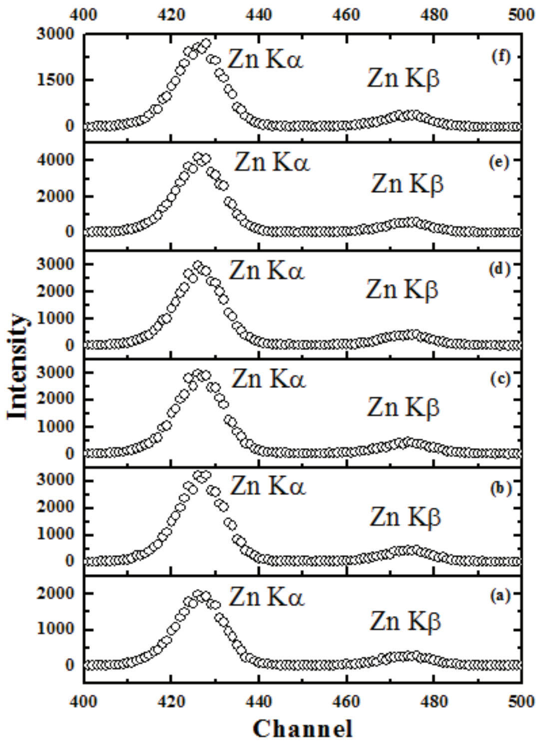

Fig. 2 EDXRF spectra of prepared different solution ZnO a) non-annealed with $ZnCl_2$ b) annealed with $ZnCl_2$ c) non-annealed with $Zn(NO_3)_2$ d) annealed with $Zn(NO_3)_2$ e) non-annealed with $ZnSO_4$ f) annealed with $ZnSO_4$

Wettability of all films was analyzed both non-annealed and annealed films. Fig. 3 and Table 2 show

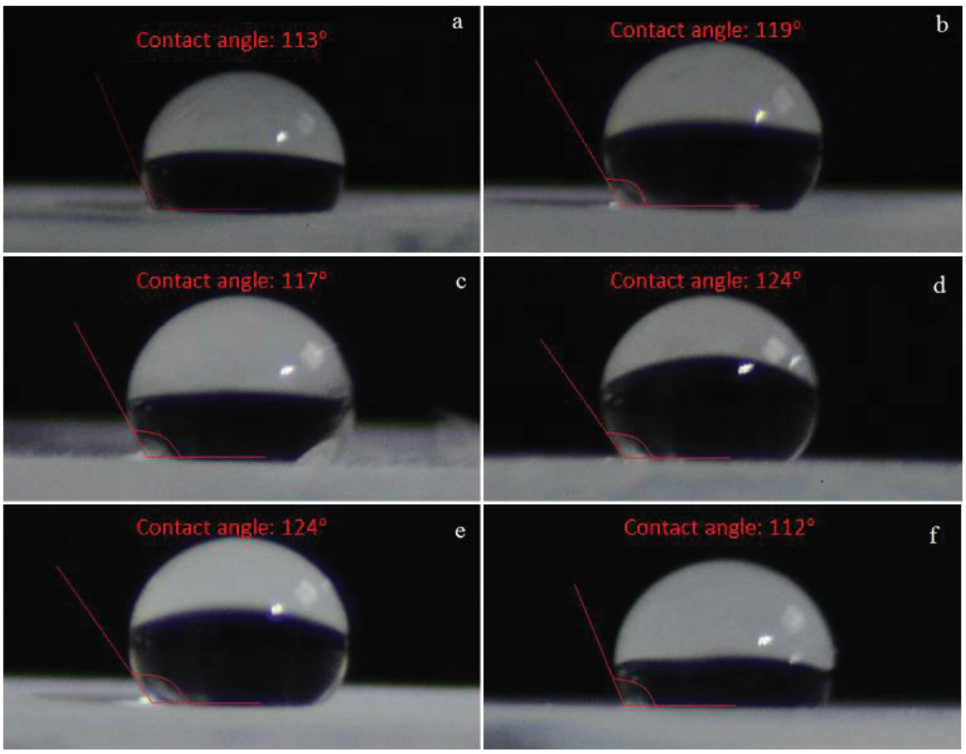

Fig. 3 Contact angles of prepared different solution ZnO a) non-annealed with $ZnCl_2$ b) annealed with $ZnCl_2$ c) non-annealed with $Zn(NO_3)_2$ d) annealed with $Zn(NO_3)_2$ e) non-annealed with $ZnSO_4$ f) annealed with $ZnSO_4$

that all films have repelling structures to water. Thus all films show hydrophobic properties. While after annealed a and c samples contact angles were increasing e sample decreasing.

Table 2. Contact angles values of ZnO films (a non-annealed and b annealed with $ZnCl_2$, c non-annealed and d annealed with $Zn(NO_3)_2$, e non-annealed and f annealed with $ZnSO_4$)

Contact angles of same sample non-annealed and annealed (degree)			
Sample	a-b	c-d	e-f
Non-annealed	113	117	124
Annealed	119	124	112

Thickness of ZnO films was calculated by the gravimetric weight difference method in terms of deposited weight of all films on the glass substrate, per unit area (g/cm^2). The thickness was calculated using formula,

$$T = \frac{M}{\rho A} \tag{10}$$

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 (ϱ = 5.61 g/cm^3) (BULAKHE *et al.* 2013). Table 3 show that the thickness of all samples raised with annealed. These sources may be raising oxygen of ZnO structures as annealing.

Table 3. Thickness values of ZnO thin films a non-annealed and b annealed with $ZnCl_2$, c non-annealed and d annealed with $Zn(NO_3)_2$, e non-annealed and f annealed with $ZnSO_4$)

Thickness of same sample non-annealed and annealed (μm)			
Sample	a-b	c-d	e-f
Non-annealed	1.04	1.78	2.01
Annealed	1.11	2.01	2.15

Conductivity of all films was measured by hot probe method and each film shown n-type conductivity.

4. Conclusion

In summary, we have presented a simple SILAR method for the growth of non-annealed and annealed three different solutions ZnO nanostructure thin films on to glass substrates. Wettability property of all ZnO films was examined and clearly demonstrates the hydrophobic behavior. This SILAR method proved to be a simple and cost effective approach to prepare hydrophobic ZnO nanostructure thin films so these finds are significance for future self-cleaning application.

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