

ALTERCATIONS IN PHYSICOCHEMICAL PROPERTIES OF SOFT CHEMICAL ROUTE SYNTHESIZED ZNO THIN FILM

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ABSTRACT

The Zinc Oxide (ZnO) thin films were deposited onto the glass substrates by a successive ionic layer adsorption and reaction method, which is based on the alternate dipping of substrate in a zinc nitrate solution complexes with NH_4OH and distilled water. These as deposited ZnO thin films are annealed at 100, 200, 300 and 400 °C respectively. the effect of annealing studied as a function of X-ray

diffraction pattern, Raman spectrum, while surface morphology and compositional analysis studied using scanning electron microscopy (SEM) and energy dispersive X-ray absorption spectra (EDAX) respectively. The X-ray diffraction (XRD) pattern shows wrurtzite structure with c axis orientation. The Raman active zone-center optical phonons predicted by the group theory are $A_1 + 2E_2 + E_1$. SEM images shows modifications in surface morphology upon annealing treatments while the exact composition as observed as expected and used for ZnO synthesis, optical absorption spectra shows two peaks at 300 and 375nm corresponding for phonon exciton formation and transitions.

KEYWORDS: ZnO thin film, SILAR, Annealing, Raman Spectroscopy.

INTRODUCTION

It known to all that ZnO is a direct band gap semiconductor with a band gap energy of 3.4 eV and it is transparent over visible wavelength region. Moreover, its conductivity can be varied from semi-insulator to a semimetal depending on its thickness and doping level. Thin Films of ZnO shows high piezoelectric and relatively high thermoelectric properties depending on

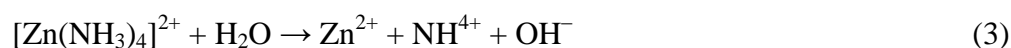
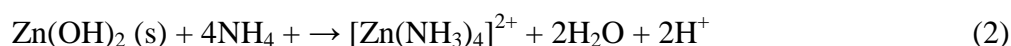
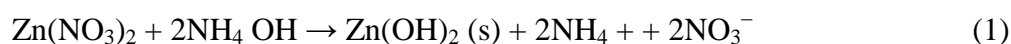
the method of synthesis applied during the preparation.^[1] Various chemical and physical processes have been developed for thin film deposition, such as conventional chemical vapor deposition (CVD), spray pyrolysis, thermal evaporation, sputter deposition technique and electro deposition.^[1,2] Like chemical bath deposition technique, the Successive Ionic Layer Adsorption and Reaction (SILAR) technique for the preparation of thin films from aqueous solution is a promising technique because of its simplicity and economics.^[1,2] It is evidenced that, solution based synthesis is best suitable method for these kind of materials.^[13, 20] The SILAR technique has many advantages such as low temperature requirement, low cost, scalability, easier handling effectiveness, simplicity, easily controlled deposition rate, deposition parameters, and thickness of the film. For synthesis of ZnO thin films, the basic building blocks are ions instead of atoms and thus, the preparative parameters can be easily controlled. The SILAR technique is also known to be a modified version of chemical bath deposition^[4, 5] Apart from effectiveness and simplicity, there are another advantages to convenient for large scale deposition mainly. The process can be approved on any kind of substrate, it does not require high quality substrates, also not require vacuum at any stage, by changing the deposition cycles, the deposition rate, thickness of the film can be easily controlled, and also it operates at low temperature. This SILAR technique is totally based on the adsorption and reaction of the ions from the solutions.^[7, 8]

There are many factors which affecting the deposition process while preparing the film such as thermal annealing, nature of substrate, PH values, quality of precursor solutions, their concentrations, individual rinsing and immersion time periods and complexing agents.^[1,2] The prepared samples are annealed at 100, 200, 300 and 400 °C to investigate the annealing effects on the structural and optical properties of ZnO NRs. The annealing processes are applied in atmospheric conditions in an ash furnace for one hour. Zinc oxide (ZnO) is an interesting wide band gap (~3.3 eV) II-VI semiconductor because exhibits numerous characteristics suited for various technological applications such as antireflection coatings, gas sensors, varistors transparent electrodes in solar cells, UV and blue light emitters, piezoelectric devices, and even thin film transistors.^[1,10]

MATERIALS AND METHOD

Cationic solutions are prepared with 0.2 M $\text{Zn}(\text{NO}_3)_2$ and the PH value of the solution is set to 10 by adding 25% ammonia solution ($\text{NH}_4 \text{OH}$). After stirred for a few minutes at room temperature, the solution becomes ready. 100 ml zinc nitrate solution complexes with

NH₄OH kept in a beaker and the substrates on which films has to be deposited under standard conditions were vertically suspended in the beaker and the solution was constantly stirred using magnetic stirrer in a water bath of constant temperature of 70 °C.^[7,8] Substrate alternate dipping into the zinc nitrate solution and warm DI water, the ZnO NRs are deposited with 50 cycles. Possible reactions occurring during the deposition of ZnO NRs are, respectively, as in Eqs. (1) to (5) [20]



SILAR method is a two-step process involving subsequent immersion of cleaned substrate in cationic (Zinc ammonia complex) for 15 second at room temperature and anionic (near boiling DI water) for 15 Second then the substrate was hanged on in the air to drying for 10 second. 40 deposition cycles were made and then the deposited ZnO films were annealing in an ash furnace for one hour and then the films are characterized.^[8, 9]

There are several studies investigated based on annealing-induced variations in the structural, morphological, electrical and optical properties of ZnO thin films. According to the results of these studies, after annealing, the crystal structures of ZnO thin films is enhanced^[1, 5] and the (002) orientation becomes weaker, while the (001) orientation becomes more prominent.^[14, 15] Furthermore, the results of XRD measurements show that the intensities of the diffraction peaks of ZnO films rise, and they shift to higher diffraction angles with annealing.^[1,16] It is also reported that the grain sizes of ZnO structures increase^[1, 14-17], while the surface roughness of ZnO films decreases.^[1, 16] The results of the study using different precursors to obtain ZnO thin films show that the crystal quality of ZnO thin films annealed at 400 °C is enhanced, and the intensities of diffraction peaks of XRD measurements are significantly increased; however, it is also noted that vacuum annealing does not change the preferential orientation of ZnO thin films.^[1,6] It is also note that increasing the annealing temperature beyond a certain value disturbs the crystal structure^[15, 6], and those new defects appear with post-annealing.^[1, 14, 19] Annealing enhances the transmittances of ZnO thin films^[17], and their values increase with the increase of the annealing temperature.^[14, 2] On the other hand, there are studies reporting decreases in the transmittances at visible

wavelengths after annealing.^[1, 18] With annealing, the emissions of ZnO films increase at UV wavelengths and decrease at blue-green wavelengths.^[1,7] In addition, after annealing, the absorption edge energies of ZnO films show a red shift.^[1]

RESULTS AND DISCUSSIONS

1. Structural characterizations

Figure 1 represent the X-ray diffraction (XRD) pattern of as deposited and annealed ZnO thin films, according to the results after annealing, the crystal structures of ZnO thin films are enhanced and the (002) orientation becomes weaker, while the (001) orientation becomes more prominent.^[14, 15] Furthermore, the results of XRD measurements show that the intensities of the diffraction peaks of ZnO films rise, and they shift to higher diffraction angles with annealing.^[16] It is also reported that the grain sizes of ZnO structures increase^[14-17], while the surface roughness of ZnO films decreases.^[16] The results of the study using different precursors to obtain ZnO thin films show that the crystal quality of ZnO thin films annealed at 400 °C is enhanced, and the intensities of diffraction peaks of XRD measurements are significantly increased; however, it is also noted that vacuum annealing does not change the preferential orientation of ZnO thin films.^[18] We also note that increasing the annealing temperature beyond a certain value disturbs the crystal structure^[15], and those new defects appear with post-annealing.^[14, 19] Annealing enhances the transmittances of ZnO thin films^[17], and their values increase with the increase of the the annealing temperature.^[14] On the other hand, there are also studies reporting decreases in the transmittances at visible wavelengths after annealing.^[7, 18] With annealing, the emissions of ZnO films increase at UV wavelengths and decrease at blue-green wavelengths.^[7, 9]

2. Raman Spectra

Understanding the specifics of phonon spectrum both optical and acoustic of ZnO material can help in using ZnO for various optoelectronic applications. The Raman spectroscopy study carried on pristine ZnO thin films is as shown in Figure 2 which represents high peak at 480 and 1450 cm^{-1} . The Raman active zone-center optical phonons predicted by the group theory are $A_1 + 2E_2 + E_1$. The phonons of A_1 and E_1 symmetry are polar phonons and, hence, exhibit different frequencies for the transverse optical (TO) and longitudinal optical (LO) mode.^[14] Nonpolar phonon modes with symmetry E_2 have two frequencies, E_2 high associated with oxygen atoms and E_2 low associated with Zn sublattice. The observed peak at 480 cm^{-1} corresponds to LO mode while the other high peak observed at 1450 cm^{-1} corresponds to TO

mode of ZnO materials. Peak at 1890 cm^{-1} confirms the powder nature of the ZnO materials, while on annealing smaller shift in the peak positions are observed.^[15]

3. Compositional analysis

Figure 3 shows the energy dispersive X-ray spectrum (EDAX) obtained from ZnO pristine and annealed thin films, from the figures, it can be seen that the peaks corresponding to Zinc (Zn) and Oxygen (O) are obtained which confirms the expected elemental tresses in thin films with nearly equal proportionate of elemental compositions as per the tabulated data therein.

4. Surface morphology

Surface morphology is one of the major contenders for deciding the material applicability in an optoelectronic device; hence, the morphology is studied using SEM as shown in Figure 4 for as deposited, 100, 200, 300, and 400°C, respectively. The homogenous granular distribution of grains can be seen on pristine thin films while on annealing treatments, the uneven homogenate granules are found to be grown which may be related to thermal polygonization.^[16] The nature of grain growth seems to be following the nature as the annealing temperature is increasing.^[17]

5. Optical study

Optical study carried out to learn electronic transition in as deposited and annealed ZnO thin films, grown at room temperature by SILAR technique. From optical absorption spectra the relationship between the absorption coefficient (α) and the photon energy ($\alpha h\nu^2$) for the direct allowed transition. By extrapolating the linear part of curve as a function of $h\nu$, the energy axis will give energy band gap (E_g). From fig. 5 energy band gap of as deposited and annealed ZnO thin film found to be 3.37eV which is very close to the reported value (3.33 eV) of the bulk ZnO.^[14] From Fig. 5 it is seen that the band gap energy decreases from 3.24 to 3.14 eV with increase in annealing temperature. For as grown samples, band gap is higher (3.24eV), it may be due to the presence of Zinc Hydroxide which might be in amorphous form. But as the annealing temperature increases, the band gap has decreased up to 3.14eV. It may be due to the removal of Zn(OH)_2 from the films and/or removal of defect levels from the films which is more common phenomena in chemically deposited thin films. Removal of stacking faults results in orientation of individual crystallites and the occurrence of defect free grain boundaries. In addition, one can relate the decrease in the band gap energy with increase in grain size. XRD analysis showed that the grain size of ZnO thin films was

increased after heat treatment. This is attributed to the grain size-dependent properties of the energy band gap.

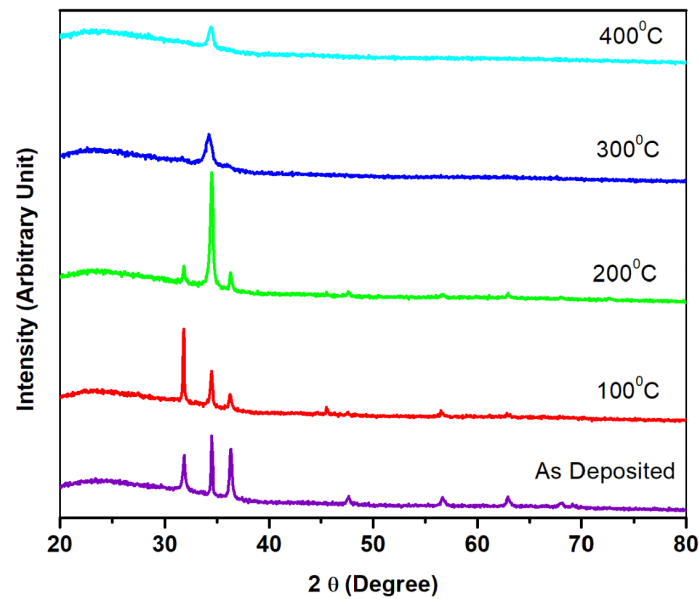


Figure 1: XRD pattern obtained from the as deposited and annealed ZnO thin films by SILAR method.

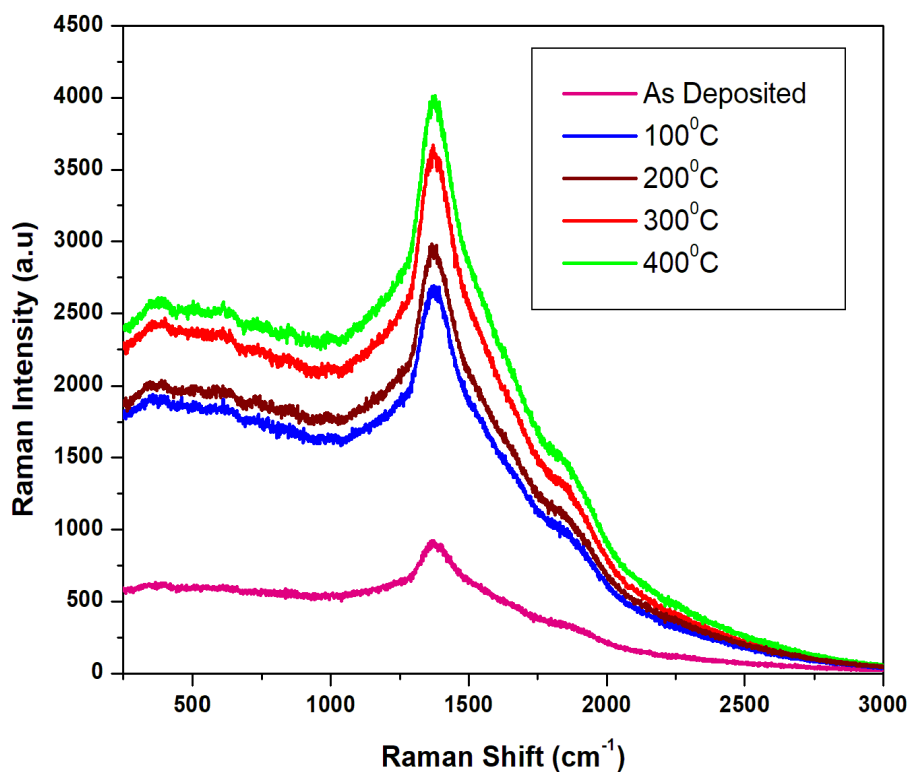


Figure 2: Raman spectra obtained from as deposited and annealed thin films of ZnO.

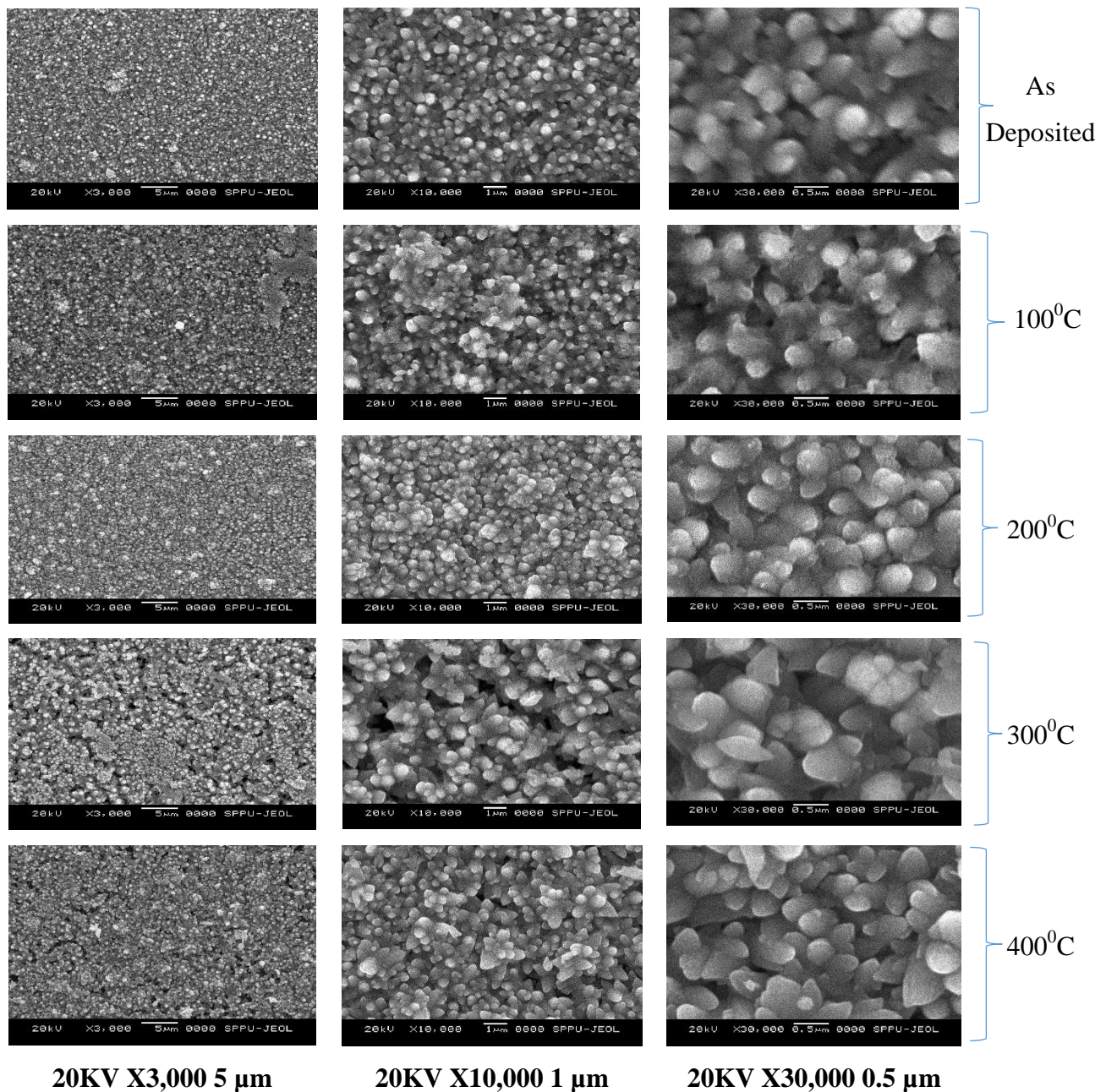


Fig 3: SEM images of as deposited and annealed ZnO thin films.

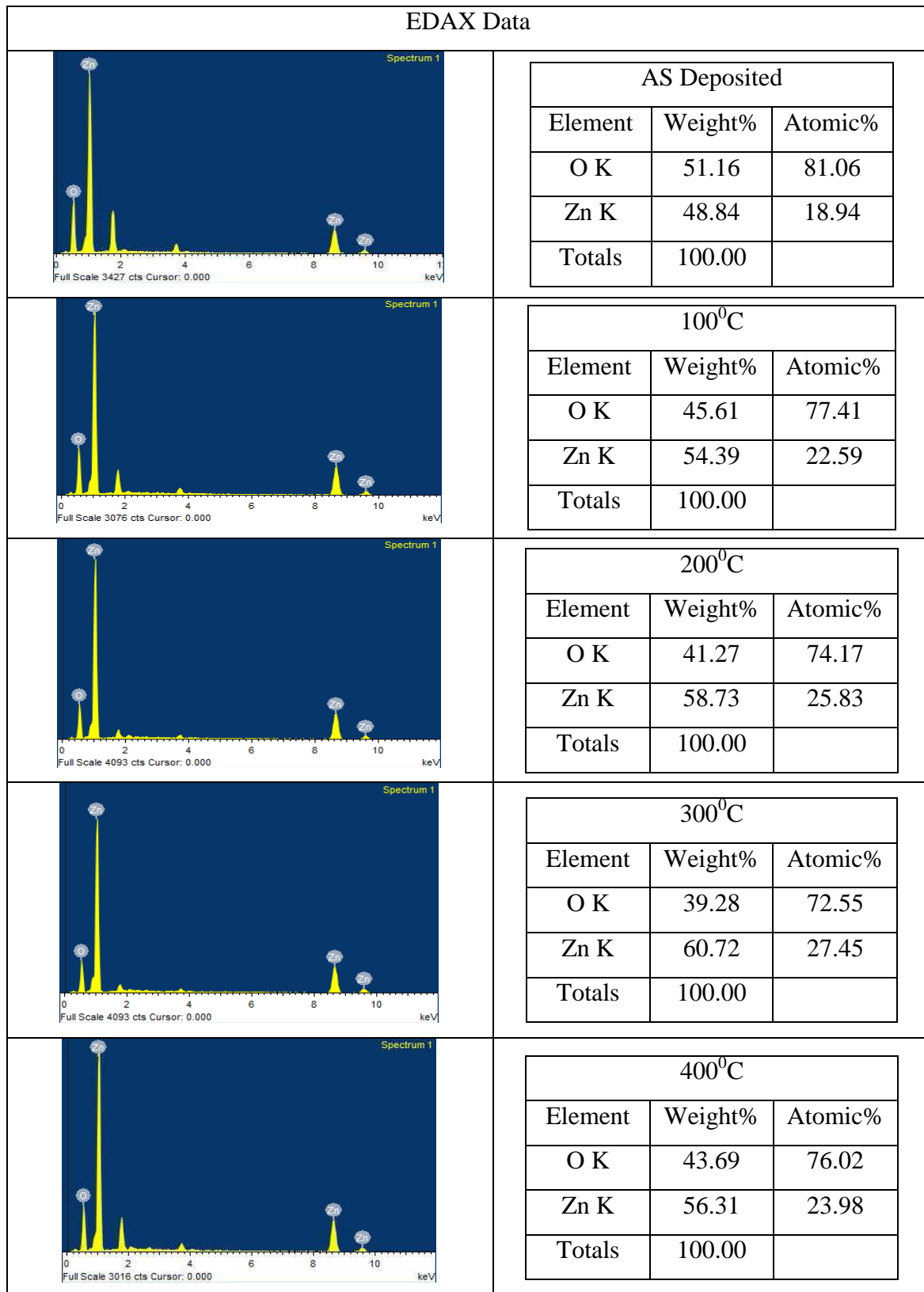


Fig 4: EDAX spectra obtained from as deposited and annealed ZnO thin films deposited using SILAR method.

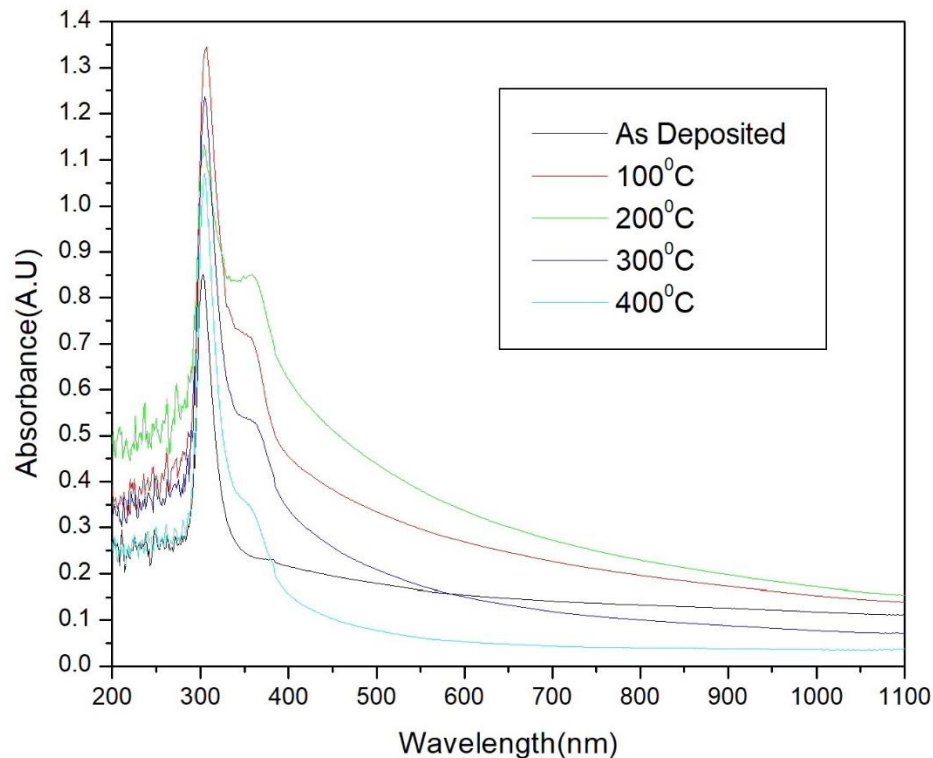


Figure 5: Optical absorption spectra obtained from as deposited and annealed ZnO thin films deposited using the SILAR techniques.

CONCLUSIONS

The results obtained from the as deposited and annealed treatment provided ZnO thin films has shown that the ZnO thin films can be successfully deposited using the SILAR techniques on glass substrates at room temperature. The annealing treatment modifies the structural, surface morphology, optical properties of the films. The annealing at 400°C found to be well suitable for alteration of physicochemical and optoelectronic properties particularly XRD shown polycrystalline nature with presence of peak confirming the crystallites size variations, the surface morphology seems to be granulized with the annealing. The optical properties exhibits increase in energy band gap on annealing which may be correlated to grain growth and segregations.

REFERENCES

1. C. Duman a and H. Guney, Influence of annealing and optical aging on optical and structural properties of ZnO thin films obtained by SILAR method, Lithuanian Journal of Physics, 2017; 57: 195–201.

2. Hiten Sarma, Dhruba Chakraborty, K.C. Sarma, Optical and structural properties of ZnO thin films fabricated by SILAR method, *International Journal of Innovative Research in Science, Engineering and Technology*, 2014; 3(10).
3. Raidou, A., Benmalek, F., Sall, T., Aggour, M., Qachaou, A., Laanab, L. and Fahoume, M. Characterization of ZnO Thin Films Grown by SILAR Method. *Open Access Library Journal*, 2014; 1: 588.
4. A. Raidou F. Benmalek T. Sall M. Aggour A. Qachaou L. Laanab M. Fahoume, The influence of rinsing period on the structural and optical properties of ZnO thin films, *Optical and Quantum Electronics*, 2013; 45: 8.
5. Haridas D. Dhaygude, Surendra K. Shinde, Ninad B. Velhal, G.M. Lohar, and Vijay J. Fulari, Synthesis and characterization of ZnO thin film by low cost modified SILAR technique, *AIMS Materials Science*, 2012; 3: 349-356.
6. A. Raidoua, M. Aggoura, A. Qachaoua, L. Laanabb, M. Fahoumea, Preparation And Characterisation of ZnO Thin Films Deposited By SILAR Method, *M. J. Condensed Matter*, 2010; 12: 2.
7. Nkrumah, F.K. Ampong, B. Kwakye-Awuah, R.K. Nkum, F. Boakye, Synthesis And Characterization Of ZnO Thin Films Deposited By Chemical Bath Technique, *International Journal of Research in Engineering and Technology*, 2019; 02: 12.
8. S. Sivapriya, K. Balasubramanian, Preparation and Characterization of ZnO Thin Films by Using Two Different Techniques, *IOSR Journal of Applied Physics*, 42-44.
9. R. D. Robinson, B. Sadtler, D. O. Demchenko, C. K. Erdonmez, L. W. Wang, A. P. Alivisatos, Spontaneous superlattice formation in nano-rods through partial cation exchange, *Science*, 2007; 317: 355-358.
10. M. Sugiyama, F. B. Dejene, A. Kinoshita, M. Fukaya, Y. Maru, T. Nakagawa, H. Nakanishi, V. Alberts, S. F. Chichibu, The use of diethylselenide as a less-hazardous source in CuInGaSe₂ photoabsorbing alloy formation by selenization of metal precursors premixed with Se, *J. Cryst. Growth*, 2006; 294: 214-217.
11. W. E. Devaney and R. A. Mickelsen, Vacuum deposition processes for CuInSe₂ and CuInGaSe₂ based solar cells, *Solar Cells*, 1988; 24: 19-26.
12. S. T. Kim, K. Kim, J. H. Yun, B. T. Ahn, A simple route to grow Cu(InGa)Se₂ thin films with large grains in the coevaporation process, *Curr. Appl. Phys.*, 2018; Doi10.1016/j.cap.2018.04.013.
13. Ravichandran, M. Vasanthi, K. Thirumurugan, B. Sakthivel, K. Karthika, Annealing induced reorientation of crystallites in Sn doped ZnO films, *Opt. Mater.*, 2014; 37: 59-64.

14. V. Shelke, M.P. Bhole, and D.S. Patil, Open air annealing effect on the electrical and optical properties of tin doped ZnO nanostructure, *Solid State Sci*, 2012; 14: 705–710.
15. S.C. Shei, P.Y. Lee, and S.J. Chang, Effect of temperature on the deposition of ZnO thin films by successive ionic layer adsorption and reaction, *Appl. Surf. Sci.*, 2012; 258: 8109–8116.
16. P.V. Rajkumar, K. Ravichandran, M. Beneto, C. Ravidhas, B. Sakthivel, and N. Dineshbabu, Enhancement of optical and electrical properties of SILAR deposited ZnO thin films through fluorine doping and vacuum annealing for photovoltaic applications, *Mater. Sci. Semicond Process*, 2015; 35: 189–196.
17. Ravichandran, P.V. Rajkumar, B. Sakthivel, K. Swaminathan, and L. Chinnappa, Role of precursor material and annealing ambience on the physical properties of SILAR deposited ZnO films, *Ceram. Int.*, 2014; 40: 12375–12382.
18. M.A. Yildirim and A. Ates, Influence of films thickness and structure on the photo-response of ZnO films, *Opt. Commun*, 2010; 283: 1370–1377.
19. H. Güney and M.E. Ertarğın, Effective annealing of ZnO thin films grown by three different SILAR processes, *East. Anat. J. Sci.*, 2015; 1: 20–24.