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Optical and Structural Characterizations of ZnO Thin Films Fabricated by SILAR Method via Sulphate Route

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Abstract: The ZnO thin films were prepared on cleaned glass substrates by SILAR deposition technique using Zn $(CH_3COO)_2$ and $Na_2S_2O_3$ as precursor solution with deposition cycles of 25, 50 and 75. The prepared samples were annealed in air. The ZnO thin films are prepared from source of sulphate precursor route followed by decomposition at 450°C annealing which leads to the properties changes. The prepared thin films were characterized for their structural, micro structural and optical properties by XRD, FESEM and UV-Visible spectroscopy. The XRD analysis shows that the prepared samples are polycrystalline and it exhibits hexagonal structure. The morphology of the ZnO thin films characterized by FESEM revealed that the film consisted of mixture of nanoparticles and the EDAX results showed the presence of ZnO in the prepared thin films. The optical properties of the deposited films were characterized by UV-VIS and FTIR spectrometry. The paper will discuss the preparation methods and results of ZnO thin films by SILAR method.
Keywords: ZnO; Nano crystalline thin film; SILAR deposition method.

1. Introduction

Zinc oxide (ZnO) is one of the most prominent binary II-VI semiconductor compounds, it is an n-type Semiconductor of hexagonal (wurtzite) structure [1].Thin films of ZnO have been prepared by different researchers using various techniques such as spray pyrolysis [2], physical vapour deposition [3], chemical vapour deposition [4], sputtering [5], sol–gel method [6] and Successive Ionic Layer Adsorption and Reaction (SILAR) [7] method. The SILAR technique involves multiple dipping of a substrate in cationic and anionic precursors. In addition to its simplicity, SILAR also has a number of advantages: a) it offers extremely easy way to dope, b) operating at room temperature c) no power requirements. The thin films and nanoparticles of ZnO used in several applications, such as in dye sensitized solar cell [8],gas sensors [9], and light emitting diodes [10].

2. Experimental

ZnO thin films were deposited by SILAR method on well cleaned glass substrate (6cm x 1.25cm x 1mm) using 0.1 mol Zinc acetate ($(CH_3COO)_2Zn\ .2H_2O$) with 0.1 mol NaOH used as source of cationic

precursor solution and sodium thiosulfate ($Na_2S_2O_3.5H_2O$) used as the source of anionic precursor solution. The SILAR deposition cycles were repeated and carried out for 25, 50 and 75 times separately to get the three desired films. The prepared films were dried at room temperature for 2 hours and then annealed in air at 450°C for 3 hours which leads to the properties changes. Optical characterizations of the films were carried out using a Unico UV-2102PCS spectrophotometer. The structural properties of the films were characterized by XPERT-PRO X-ray powder diffractometer (CuKa radiation, 0.15418 nm). Surface morphology was characterized by FE-SEM 6701 F (Resolution 6 xlac).

3. Results and Discussion

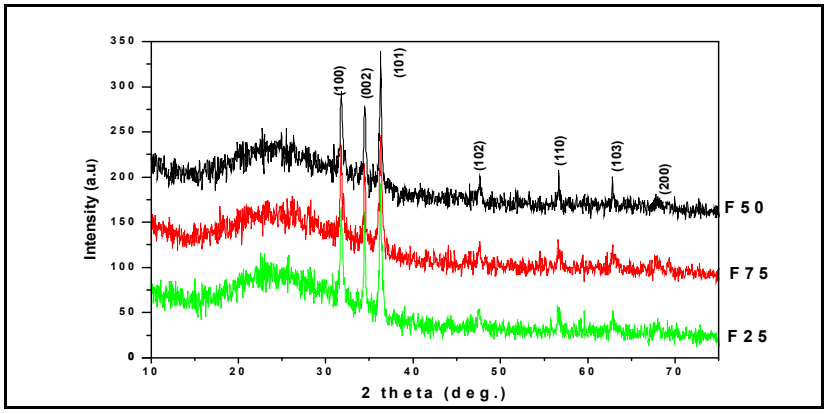

Fig. (1) XRD pattern of ZnO thilms prepared for various (25, 50 and 75) deposition cycles.

Figure 1 shows X-ray diffraction pattern of ZnO thin films prepared at three different deposition cycles of 25, 50 and 75. The XRD pattern shows hump around 25º two theta corresponds to amorphous glass substrate, the sharp peaks are entire characteristic of the hexagonal ZnO wurtzite structure according to JCPDS card file No. 36-1451. No other peaks are observed, suggesting that only single-phase ZnO has formed. The lattice parameter values, *a* and *c*, have been calculated for 25,50 and 75 deposition cycles from their accurately determined two theta positions with UNITCELL least minimisation code (11).

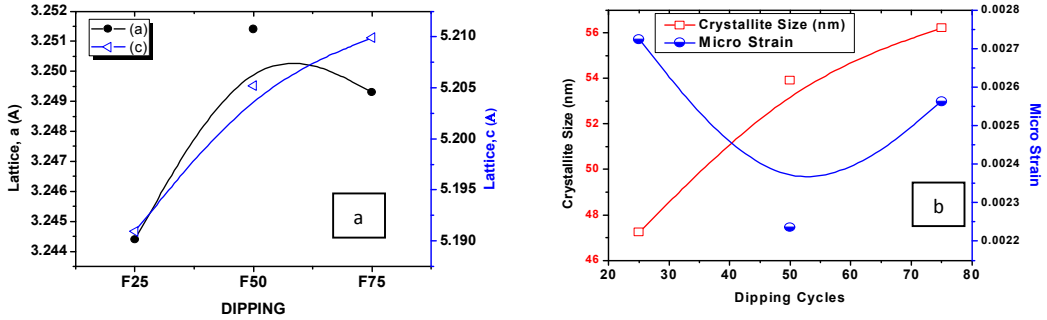

Fig.2 shows the variation of (a) lattice parameters with the deposition cycles and (b) crystallite size and micro strain with the deposition cycles.

Lattice parameter values, *a* and *c* are in good agreement with the reported standard values (JCPDS No. 36-1451). The standard ZnO lattice parameters were a=3.250 Å and c=5.207 Å (12). The lattice parameter of 50 cycles of dipping sample almost well agreed with standard ZnO lattice parameter, whereas the other two samples show either low in *a* parameter or high in *c* parameter. The average crystallite size of the SILAR deposited ZnO thin films has been calculated using Scherer formula[13] shown in equation (1) and the average lattice strain has been calculated using Stokes Wilson equation [14] shown in equation (2). The FWHM values of the samples were derived from their highest intensity peak broadening by pseudo-voigt peak fitting.

Crystallite size $D_{ave} = 0{\cdot}94\lambda/\beta \cos\theta$, ----- (1) and Micro *Strain* $\varepsilon = \beta/4\tan\theta$ ----- (2)

Where D_{ave} is the mean crystallite size, ε is the average micro strain *(□d/d),* β the full width at half maximum of the diffraction line, θ the angle of diffraction, and λ the wavelength of the X-ray radiation. The crystallite sizes obtained were ~ 47 nm, 54 nm and 56 nm for deposition cycles 25, 50 and 75 respectively.

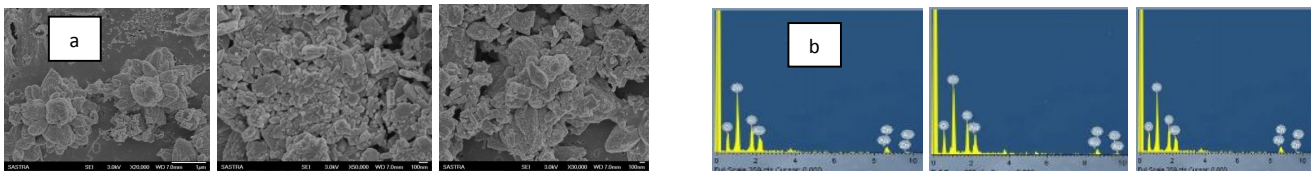

Fig.3 (a) and (b) shows the FESEM and their EDAX spectra of ZnO films by SILAR method for 25 dippings, 50 dippings and 75 dippings

Field Emission Scanning Electron Microscope (FESEM) images and their corresponding EDAX spectra of ZnO films deposited for different deposition cycles 25,50 and 75 are shown in figures 3(a) and (b) and (c). The size distribution of grains appears to be less homogenous for 25 deposition cycles, which shows distinguished micro flower shape composed with self-aligned prismatic nanoparticles and grown film not fully covered the substrate. An organized change occurs in the structure from micro-flower nanostructure to a less uniform surface with closely attached nano particles in 50 and 75 deposition cycles. Agglomeration of nano particles also seems to be present in the certain region on the ZnO film surface. The EDAX results of the ZnO thin film clearly indicated the chemistry of the film. It was observed that the UV-Visible transmittance of the film was high in 25 deposition cycles. The optical band gap of the films were calculated using Tauc plot method ($(\alpha h\nu)^2$ against $h\nu$) and found to be 3.01eV for 25 deposition cycles, 3.31ev for 50 deposition cycles and 3.22 eV for 75 deposition cycles respectively.

4. Conclusions

ZnO nanocrystalline thin films have been synthesized by SILAR method using zinc acetate and sodium thiosulfate. The XRD analysis reveals that ZnO is crystalline nature and in hexagonal structure, with the nanoparticles of size in the range of ~47-56 nm. The result of UV-Vis. spectrum shows that prepared ZnO thin films have UV absorption ability. EDAX analysis of the prepared ZnO thin films confirms that the samples are composed of Zn and O without any impurity. SEM micrograph witnesses the samples consist of regular and almost spherical shape particles at higher deposition cycles and the films are homogeneous and well covered to the substrate. The data presented here concludes that in SILAR method, the number of deposition cycles plays an important role in fabrication of good quality ZnO nanocrystalline thin films and also determining the particle size.

5. References

1. A Mang, K Reimann and St Rubenacke, Solid State Commun. 94, 251 (1995)
2. Ayouchi R, Leinen D, Martín F, Gabas M, Dalchiele E and Ramos-Barrado J R 2003 Thin Solid Films 426 68
3. Kouam J, Ait-Ahcene T, Plaiasu A G, Abrudeanu M, Motoc A, Beche E and Monty C 2008 Solar Energy 82 226
4. Wang X H, Li R B and Fan D H 2011 Appl. Surf. Sci. 257 2960
5. Zhang Zhonghai, Hossain Md Faruk, Arakawa Takuya and Takahashi Takakazu 2010 J. Hazard. Mater. 176 973
6. Yakuphanoglu Fahrettin 2010 J. Alloys Compd. 507 184
7. X.D. Gao, X.M. Li, W.D. Yu, J. Solid State Chem. 177 (2004) 3830.
8. Wu Jih-Jen, Chen Guan-Ren, Yang Hung-Hsien, Ku Chen-Hao and La Jr-Yuan 2007 Appl. Phys. Lett. 90 213109
9. Chen Jin, Li Jin, Li Jiahui, Xiao Guoqing and Yang Xiaofeng 2011 J. Alloys Compd. 509 740
10. Kim K, Horwitz J S, Kim W H, Makinen A J, Kafafi Z H and Chrisey D B 2002 Thin Solid Films 420–421 539.
11. T J B Holland and S A T Redfern "Unit cell refinement from powder diffraction data: the use of regression diagnostics". Mineralogical Magazine 61 (1997) 65-77.
12. Abrahams, S., Bernstein, J. Acta Crystallogr, Sec. B 25, 1233 (1969)

13. Maleki M, Ghamsari M Sasani, Mirdamadi Sh. and Ghasemzadeh R 2007 Semicond. Phys. Quant. Electron. Optoelectron. 10 30.
14. Ajaya Kumar Singh, Swati Mehra, Gautam Sheel Thool.European Chemical Bulletin 2013, 2(8), 518-523.

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