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Studies on undoped and doped zinc oxide thin films grown by chemical solution dip technique for photovoltaic and gas sensors

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Abstract:

In recent years, Intensive investigations are going on not only in the field of basic thin film physics, but also in material science, thin film circuit designs, production engineering concerning thin films, etc.., to cope with the demand of industries . film properties are also sensitive not only to their structures but also to many parameters including thickness especially in thin film regions, hence a stringent control of the latter is imperative for reproducible electronic, dielectric optical and other properties. Zinc oxide has become a particularly interesting metal oxide material because of its unique properties. ZnO is a semiconductor with a wide band gap (3.3 eV), large exciton binding energy, abundant in nature and environmentally friendly. These characteristics make this material attractive for many applications such as solar cells, optical coatings, photo catalysts, antibacterial activities, electrical devices, active medium in UV semiconductor lasers and in gas sensors, solid state emission, chemical sensors, piezoelectric transducers, transparent electrodes, photo-catalysts, electroluminescent devices. Doping of nano materials with sutable impurities such as In and Al, has given rise to a new class of nano materials whose structural, optical and electrical properties differ from those of the corresponding host nano-materials. ZnO thin films are prepared by different techniques such as metal organic chemical vapor deposition, sol–gel, thermal evaporation, oxidation and anodizing. This paper prescribe to undoped, cadmium doped ZnO(CZO) and Aluminium doped ZnO(AZO) thin films by a chemical solution grown double dip technique for fabrication of a gas sensors and photovoltaic.

Key words: ZnO, cadmium doped ZnO(CZO, Aluminium doped ZnO(AZO), Chemical solution, dip-coating technique, XRD, SEM, AFM,PL

1.Introduction

Zinc Oxide is an inexpensive n-type semiconductor having direct band gap of 3.3 eV which crystallizes in hexagonal Wurtzite structure (c = 5.025 and a = 3.249).Thin films of Zinc Oxide (ZnO) have been widely used as Bulk Acoustic Wave Devices (BAW) and Surface Acoustic Wave Devices (SAW). Due to large exciton binding energy of 60 meV, they have potential application in Optoelectronic devices such as in solar cells, Optical wave guide, Light emitting diodes (LED). Zinc Oxide thin films are applied in Thin Film Transistors (TFT) and have been recognized as Spintronic material. It has also application in gas, chemical and biological sensors. Thin films of Zinc oxide can be prepared by various techniques; among them are Sputtering, Chemical Vapor Deposition (CVD), Laser ablation, Sol-gel, Spray pyrolysis. Sol-gel process has the advantages of controllability of compositions, simplicity in processing and is cost effective. Hence, we have used Sol-gel spin coating technique for the film preparation. Depending on the application, Zinc Oxide (ZnO) films have been subjected to various types of doping .They include Aluminum, Indium, Gallium, Manganese and Yttrium. There have been some studies on Li doped ZnO film. This paper provides detail investigation on cadmium and aluminium doped ZnO film and analyzed its transmission spectrum to evaluate film thickness and optical constants by chemical solution dip coating method.

2. Materials and Method

The present work is a preparation and characterization of undoped ZnO, Cd doped ZnO (CZO) and Al- doped ZnO (AZO) thin films by chemical deposition technique. In which the influence of solution concentration, solution pH value, film thickness, annealing temperature and concentration of Cadmium and aluminium atoms of the grown films are investigated. In addition it demonstrates that any dopant can be used in principle along with the precursor to enable them to be included in the system. The technique can be tuned to get the desired morphology and nano crystallites of desired sizes distributed over any type of substrate for various applications.

2.1 Choices and cleaning of substrate

To form the thin film with defined electrical parameters, the substrates must be smooth and flat otherwise electrical and optical properties may be affected. Therefore in choosing a suitable substrate, in addition to considering the need to provide the mechanical support to the deposits, due consideration must be given to the possible influence of the substrates on the properties of the deposits. Commonly used substrate materials for polycrystalline thin film circuits include alumina, glass, silicon and metals, beryllium oxide based ceramic, aluminium nitride.

However any type of substrate may be used in this simple growth method. Substrate cleaning in thin film technology is an important step prior to deposition. It is necessary to remove the contaminants that would otherwise affect the properties of the film.

The film thickness could be varied by varying the number of dipping. A linear increase in thickness with a growth rate of 0.016 μm per dipping was observed in the present experiment. The film thickness was also checked against cross-sectional SEM.

3. Experimental

3.1 Growth of nanocrystallites of undoped and doped ZnO

A schematic diagram of the shape-selective synthesis of doped and undoped metal oxide nanostructures via double dip technique is shown in Fig. 1. Preparation of undoped and doped ZnO nano thin films ZnO thin films were performed using a two-step chemical bath deposition technique using a solution comprising of high purity zinc sulphate, magnesium sulphate and sodium hydroxide with a pH value of 9 as first step and a dip in hot water kept near boiling point as the second step. Before deposition, the glass substrates were cleaned by chromic acid followed by cleaning with acetone. The well-cleaned substrates were immersed in the chemical bath for a known standardized time followed by immersion in hot water for the same time for hydrogenation. Possible formation mechanism the process of solution dip followed by hot water dipping (step 2) is repeated for known number of times. According to the following equation, the complex layer deposited on the substrate during the dipping in sodium zincate bath will be decomposed to ZnO due to subsequent dipping in hot water. The proposed reaction mechanism for undoped ZnO is according to the following Equation.

$ZnSO4 + 2\ NaOH \rightarrow Na2ZnO2 + H2SO4 \uparrow$.... (1)

$Na2ZnO2 + H2O \rightarrow ZnO + 2\ NaOH$ .... (2)

Part of the ZnO so formed was deposited onto the substrate as a strongly adherent film and the remainder formed as a precipitate. The addition of Metal sulphate in the ratio of Zn: Metal as100:1 in the first dip solution leads to the formation of MZO films. ZnO thin films were prepared using double dip technique shown in Fig. 1 by varying deposition parameters such as solvent medium, solution pH, concentrations, temperature, number of dippings, etc., The effect of these parameters are studied using various characterizations and the optimized deposition parameters are arrived for undoped ZnO thin films. The ‘Al ‘and ‘Cd’ doping were carried out by adding the respective metallc salts in the solution bath at different proportions (Zn : M as 100 : 1 or 10 : 1 where M =’ Cd’ or ‘Al’.

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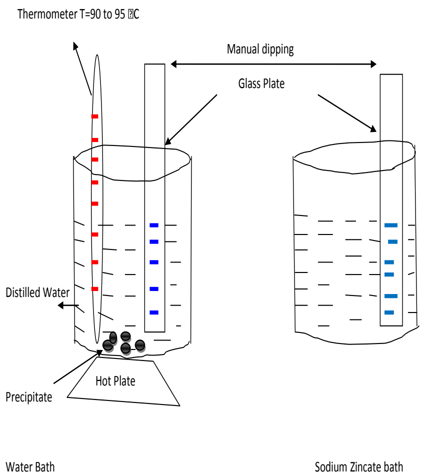

Fig. 1. Schematic representation of solution dip technique

4. Results and Discussion

4.1 Growth conditions

The growth conditions have been optimized by us for various dopants including non metals. Several parameters involved in this technique offer wide range of selection of parameters. It is found that the films deposited at room temperature are found to be smooth and uniform and compatible with any physical or chemical techniques.

Sample	Value along (002) plane	FWHM	d-spacing(Å)	Particle size (nm)	Dislocation density x 1014
Pure ZnO	34.3510	0.1757	2.60854	47	4.52
Cd doped ZnO	34.4077	0.2696	2.60437	31	9.76
Al doped ZnO	34.5648	0.3297	2.59289	25	16.00

Table.4.1 FWHM, d-spacing, particle size and dislocation density of bare and doped ZnO films.

4.2 Structural Characterization

The crystal structure and orientation of the undoped and doped ZnO thin films were investigated by taking X-ray diffraction (XRD) patterns The XRD spectra for ZnO thin films shown in Fig. 4.2 have diffraction peaks corresponding to (100), (002), (101), (102), (110), (103), (112) and (201) planes and these are observed in both bare and doped ZnO films. Cadmium doped films are less crystalline compared to bare and aluminium doped films which is revealed based on the intensity of peaks observed. Aluminium doped ZnO thin film is more crystalline than the other two films as the dominant (002) peak is having the hi ghest intensity.

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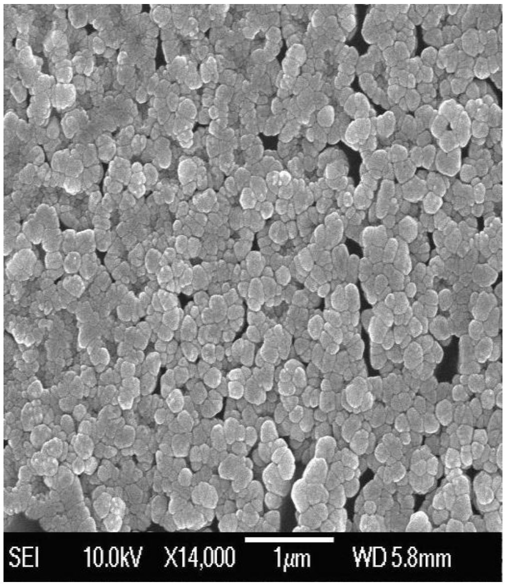
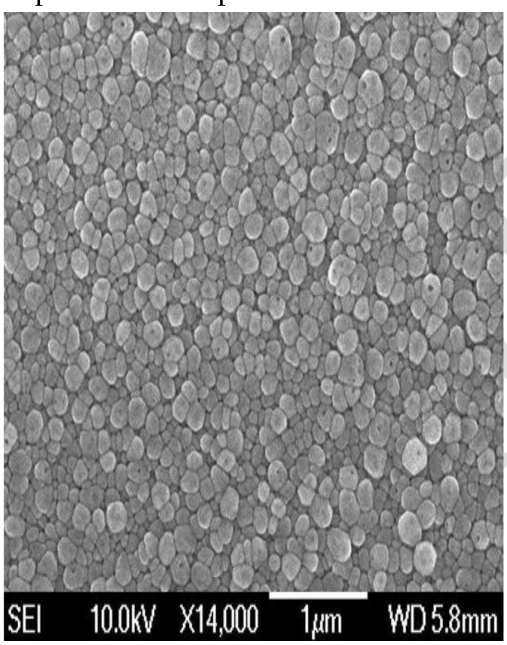


Figure 4.2 a. XRD patterns of pure and doped ZnO nanoparticles



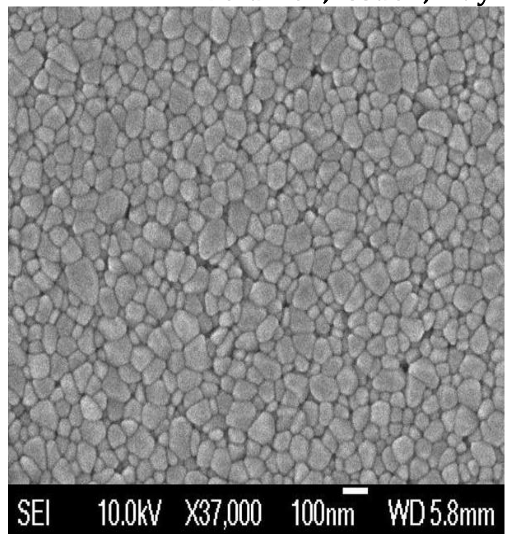


Figure 4.2.b: SEM images of Pure, Cd doped and Al doped ZnO nanoparticles

4.3 Structural Studies

Structural studies of un doped, CZO and AZO thin films reveal several interesting features. The following observations are made from X-ray diffraction studies on ZnO thin films.

a) The films deposited at room temperature are found to be uniform, the layers are better crystallized and exhibit semiconducting properties.
b) The characteristics X-ray powder diffraction of the definite compounds are visible for hot water temperature at 95*c.
c) When the films are kept annealed at high temperatures greater than 500* c the layers are found to be peeling off.

4.4 Compositional Studies

It is observed from EDX studies that nearly stoichiometric ZnO,CZO and AZO can be formed by adjusting the bath composition as 0.1mM and 0.3mM respectively. The EDX studies indicated stoichiometric Zno and optimum doped concentration for films deposited at optimized conditions. The EDX srudies indicated that the metallic sites are chosen by the deposit metallic ions. The EDZ revealed that the film composition could be altered up to a certain extent only using this method.

4.4 Morphological Studies

In summary, the synthesis and optimization of undoped and doped ZnO systems have been reported. The Morphological studies through AFM and SEM reveal's excellent feature associated with nano crystallites of which the structure is made. The SEM reveals continuously stacked nanorods of diameter ranging from 20nm to few hundred nanometers. The AFM studies reveal the surface to be of minimum roughness composed of spherical and hexagonal shaped grains. They are uniformly distributed throughout the surface exhibiting the superiority of the films. Extensive characterizations on the structure, microstructure optical and electrical properties have been made and the exotic choice available in this simple method has paved way for the synthesis of many similar systems by our group like Fe, Mg and Mn doped ZnO thin films and other TCO systems like CdO, etc. Also the properties of these thin film nanocrystallites can be tailored to suit variety of applications like, phosphors, display panels, thermal conduction and opto electronic devices. The technique is easy for automation and anticorrosive coatings can be coated employing doped ZnO systems on to various mechanical spares. The potential of this technique is yet to be exploited in full by the industrial community. The crystallite shape and size control is also feasible in this excellent method.

4.5 Optical studies

Optical absorption indicated the shift in band gab from around 3.24 to 3.15 eV due to doping and refractive index to be around 2.34 to 2.29. The transmittance become higher for AZO films with increase in doping concentration.

5. CONCLUSION

1.synthesis ZnO, Cd – doped (CzO) and AL-doped (AzO) thin films by solution grown double dip technique and optimize the preparatory conditions for device applications.

2. Characterize the films for annealing, structural, electrical, optical morphological behavior.

3.Analyze the viability of using the films for photovoltaic, gas sensor applications. Thin films of ZnO,CZO,AZO thin films are prepared by solution grown by double dip technique from aqueous solution of $ZnSO_4$. The films prepared are found to be compact and homogeneous. The deposition conditions are optimized to obtain uniform, thin film suitable for gas sensor applications. The optimized deposition conditions to prepare Zno films barh deposition conditions.

References

1. Ashrafi, A.B.M.A., Ueta, A., Avramescu, A., Kumano, H., Suemune, I., Ok, Y.-W.
and Seong, T.-Y. (2000) Applied Physics Letters, 76, 550.

2. Bates, C.H., White, W.B. and Roy, R.(1962) Science, 137, 993.

3. Baumann, H.F. & G.H. Gilmer: 3D modelling of sputter and reflow processes for interconnect metals, IEDM 1995 ,p. 89.Chou, B.C.S. et al: Fabrication of low-stress dielectric thin-film for microsensor applications, IEEE EDL, 18 (1997), 599.

4. Cote, D.R. et al: Low-temperature CVD processes and dielectrics, IBM J. Res. Dev., 39 (1995), 437. Fang, W. & C.-Y. Lo: On the thermal expansion coefficients of thin films, Sensors Actuators, 84 (2000), 310.

5. Guckel, H. et al: Fine-grained polysilicon films with build-in tensile strain, IEEE TED, 35 (1988), 800. Hansen, M. & K. Anderko: Constitution of Binary Alloys, 2nd ed., McGraw-Hill, 1958.

6. Hilleringmann, U. & K. Goser : Optoelectronic system integration on silicon: waveguides, photodetectors, and VLSI CMOS circuits on one chip, IEEE TED, 42 (1995), 841.

7. Kang, U. et al: Pt/Ti thin film adhesion on SiNx /Si substrates, Jpn. J. Appl. Phys., 38 (1999), 4147. Laurila, T. et al: Failure mechanism of Ta diffusion barrier between Cu and Si, J. Appl. Phys., 88 (2000), 3377.

8. Kim, S.-K., Jeong, S.-Y. and Cho, C.-R. (2003) Applied Physics Letters, 82, 562.

9. Murarka, S.P.: Metallization, Theory and Practice for VLSI and ULSI, Butterworth-Heinemann, 1993. Ohring, M.: The Materials Science of Thin Films, Academic Press, 1992.

10. Raaijmakers, I.J. et al: Microstructure and barrier properties of reactively sputtered Ti-W nitride, J. Electron.
11.Rossnagel, S.M. et al: Thin, high atomic weight refractory film deposition for diffusion barrier, adhesion layer and seed layer applications, J. Vac. Sci. Technol., B 14 (1996), 1819.nSmith, D.L.: Thin-film Deposition, McGraw-Hill, 1995.

12. (1990), 1221. Ritala, M. et al: Perfectly conformal TiN and Al2O3 filmdeposited by atomic layer deposition, Chem. Vapor Deposit., 5 (1999), 7.

13. Thornton, J.A.: The microstructure of sputter-deposited coatings, J. Vac. Sci. Technol., A4(6) (1986), 3059. 3 Leszczynski, M., Suski, T., Perlin, P., Teisseyre, H., Grzegory, I., 8. Bockowski, M., Jun, J., Porowski, S., Pakula, K., Baranowski, J.M., Foxon, C.T. and Cheng, T.S. (1996) Applied Physics Letters, 69, 73.