

Sol Gel Synthesis of ZnO Nano Structures by Dip Coating Method

Baskar R.S

VELTECH -Avadi, Chennai-600062

Abstract - Zinc oxide thin films were synthesized by solgel and prepared by chemical dip coating using $\text{Zn}(\text{CH}_3\text{COO})_2$ as a precursor solution. Transparent and conducting oxides thin films are a key component of many important devices such as solar cells, displays, thin film transistors and sensors. Nanometer sized nanowires offer a vehicle for the study of size-dependent phenomena. While quantum-size effects are commonly expected and easily predicted; size reduction also causes more atoms to be closer to the surface. X-ray diffraction(XRD) analysis, SEM images and EDAX as well VSM of the films confirm that all the films are of polycrystalline zinc oxide in nature possessing hexagonal wurtzite structure.

Index Terms- Zincoxide, Exciton binding energy, Thinfilms, Nanomaterials, Solgel.

I. INTRODUCTION

Zinc oxide (ZnO), a II-VI direct wideband gap semiconductor, has been studied by the scientific community since 1930. Although it has unique and interesting properties, such as a relatively high exciton binding energy (60meV), and a wide bandgap (3.34eV), and is piezoelectric, biologically safe and biocompatible. Researchers' work with ZnO has previously been focused on obtaining stable p-type dopants for ZnO.

In addition to these excellent properties ZnO possesses a large number of extrinsic and intrinsic deep-level impurities and complexes (clusters) that emit light of different colours, including violet, blue, green, yellow, orange and red, *i.e.*, all constituents of white light. Because of this, ZnO is considered to be attractive for applications requiring luminescent materials. ZnO, especially in its nanostructure form, is currently attracting intense global interest for photonic applications. ZnO has the additional advantages of being easy to grow and possessing the richest known family of nanostructures.

Zinc oxide (ZnO) has a stable wurtzite structure with lattice spacing $a = 0.325\text{nm}$ and $c = 0.521\text{nm}$. It has attracted intensive research effort for its unique properties and versatile applications in transparent electronics, ultraviolet (UV) light emitters, piezoelectric devices, chemical sensors and spin electronics. Invisible thin film transistors (TFTs) using ZnO as an active channel have achieved much higher field effect mobility than amorphous silicon TFTs. These transistors can be widely used for display applications. ZnO has been proposed to be a more promising UV emitting phosphor than GaN because of its larger exciton binding energy (60meV). This leads to a reduced UV lasing threshold and yields higher UV emitting efficiency at room temperature.

Surface acoustic wave filters using ZnO films have already been used for video and radiofrequency circuits. Piezoelectric ZnO thin film has been fabricated in to ultrasonic transducer arrays operating at 100MHz. Bulk and thin films of ZnO have demonstrated high sensitivity for toxic gases. Vanadium doped *n*-type ZnO films also demonstrate a Curie temperature above room temperature.

ZnO is of great interest for various photonic and electrical applications due to its unique physical and chemical properties, such as a wide bandgap (3.37eV), large exciton binding energy (60meV) at room temperature, piezoelectricity, and surface chemistry sensitive to environment. Applications of ZnO include light-emitting diodes [1], diode lasers [2], photo diodes[3], photo detectors [4], optical modulator waveguides [5], photovoltaic cells[6], phosphor[7], varistors [8], data storage [9], and biochemical sensors[10]. Nano structured ZnO, nano rods or nanowires in particular, has attracted intensive research, primarily for their large surface area for applications relying on heterogeneous reactions such as sensors and detectors [4], their light confinement form a nano-lasers[2], and their enhanced freedom in lateral dimensions for more sensitive piezoelectric devices[11].

Based on these remarkable physical properties and the motivation of device miniaturization, large effort has been focused on the synthesis, characterization and device applications of ZnO nanomaterials. An assortment of ZnO nanostructures, such as nanowires, nanotubes, nanorings, and nano-tetrapods have been successfully

grown via a variety of methods including chemical vapour deposition, thermal evaporation, and electro deposition *etc.*

Even though research focusing on ZnO goes back many decades, the renewed interest is fuelled by availability of high-quality substrates and reports of *p*-type conduction and ferromagnetic behavior when doped with transition metals, both of which remain controversial. Various fabrication techniques have been established for the growth of ordered ZnO nanorods and nanowires. Vapor-liquid-solid growth [2], chemical vapor deposition [12], thermal evaporation [13], carbo thermal evaporation [14], aqueous solution growth [15], flux growth [16], template-based synthesis [17], and electrochemical deposition [18–20] have all reported to successfully grown ZnO nano rod arrays. Well-aligned arrays of ZnO nanorods were grown by vapor-phase process at high temperature on the single crystal substrates such as Si [21], GaN [22], and sapphire [2], which have crystallographic similarity to ZnO. This method has limitation to scale up the process because of expensive single crystal substrate and high processing temperature. Aligned arrays of [001] ZnO nanorods on glass and silicon substrates have also been readily grown from aqueous solution with nano crystal seeding [23]; the alignment of nanorods was achieved by evolution selection growth, i.e., the crystal orientation with the higher growth rate and perpendicular to the substrate surface will survive and continue to grow [24]. Low temperature hydro thermal method has also been demonstrated to grow high quality ZnO nanowire arrays [25].

However, obtaining ZnO films with superior optical and electrical properties suitable for device applications is still a technological challenge. Several new approaches, use of variety of substrates and experimental conditions are enabling a wide range of optical and electrical properties in ZnO thin films.

In this paper, an attempt has been made to prepare study and compare the properties of ZnO thin films on glass substrate using dip coating method with the other existing literatures.

II. MATERIALS AND METHODS

The films were deposited on glass substrates (microscope slides) by dip coating technique. The substrates were cleaned, before deposition, with freshly prepared chromic acid, followed by detergent solution and distilled water. The precursor used were of AR grade and used without further purification. The precursor solution used was of

0.1M concentration of high purity zinc acetate ($\text{Zn}(\text{CH}_3\text{COO})_2$) prepared in distilled water and stirred continuously for 1 hour at room temperature. This solution is taken in a beaker and the pH was maintained around 8.

Another beaker is filled with hot water at a temperature of 70-75° C. the cleaned glass plate was first dipped in Zinc acetate solution for fraction of seconds and then immersed in hot water solution. This process is repeated for 50 times. These films were then heat treated in hot air oven at a temperature of 150°C and used for characterization studies. The deposited films were characterized using X-ray diffraction, Field Emission Scanning Electron Microscope (FE-SEM) and EDAX as well VSM to observe the magnetic behavior of ZnO.

III. RESULTS AND DISCUSSION

The synthesized ZnO films were characterized by X-ray diffraction (XRD), Field Emission Scanning Electron Microscope (FE-SEM) and EDAX.

The XRD spectra (Fig.1) of synthesized ZnO films shows hexagonal wurtzite structure and its morphology shows nanorods confirmed by FE-SEM analysis which compares well with that of the literature (26). Preetam Singh et al (27) found that the films deposited on glass at the substrate temperature (T_s) of 200°C were polycrystalline with no preferred orientation. XRD pattern of the films deposited below $T_s=300^\circ\text{C}$ show (100), (002) and (101)

Reflections. Similar kind of result is observed in the XRD pattern of the ZnO films deposited by dip coating below 200°C.

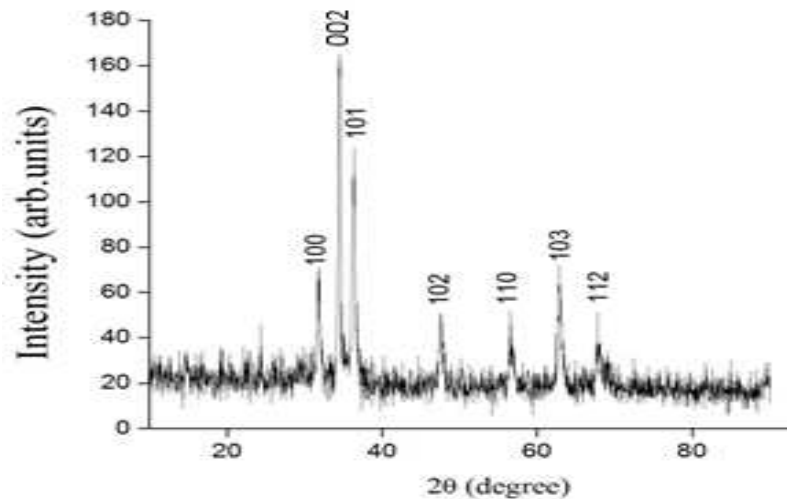


Figure1: The X-Ray spectrum of the prepared ZnO rods

The crystallite size (d) of the samples was calculated using Scherrer formula [28] $d = 0.9\lambda / \cos \theta$ where, λ is the X-ray wavelength (1.54056 Å), θ is Bragg diffraction angle and $\Delta 2\theta$ is line width at half-maximum respectively. The most prominent peak observed corresponds to (002) plane. Other planes corresponding to (100), (101), (102), (110), (103), etc. are also observed with low relative intensities. The lattice spacing was found to be $a = 0.321$ nm and $c = 0.521$ nm.

The EDAX patterns (Fig. 2) observed also confirm the presence of Zn and O in the samples prepared which is similar to the results given by N.S. Nirmala Jothi et al [30].

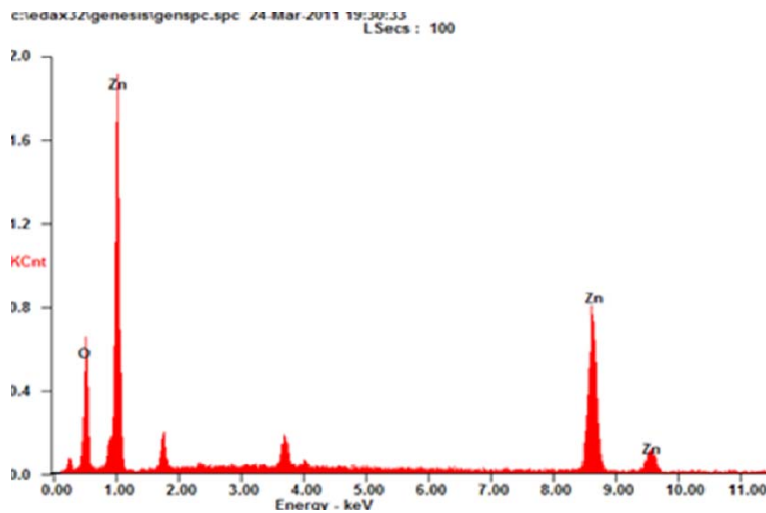


Figure2: The EDAX pattern of the prepared ZnO rods

The SEM image of the as prepared thin films are shown below in(Fig3 (a), 3(b) and3(c)), The SEM studies clearly shows that the as prepared ZnO film exhibits good morphology as compared with the literature(29) which clearly depicts the preparation of ZnO film by a simple dip coating method is effective and useful.

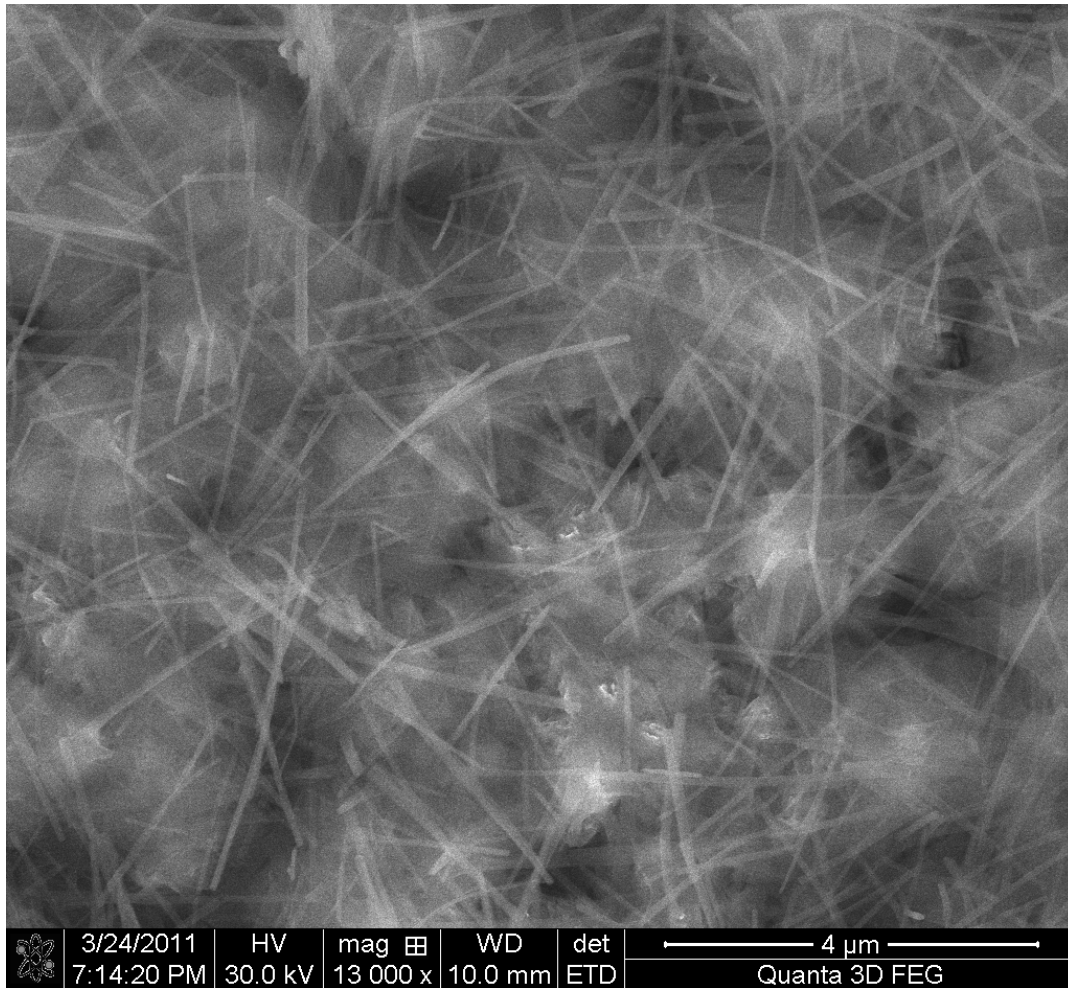


Fig.3(a)

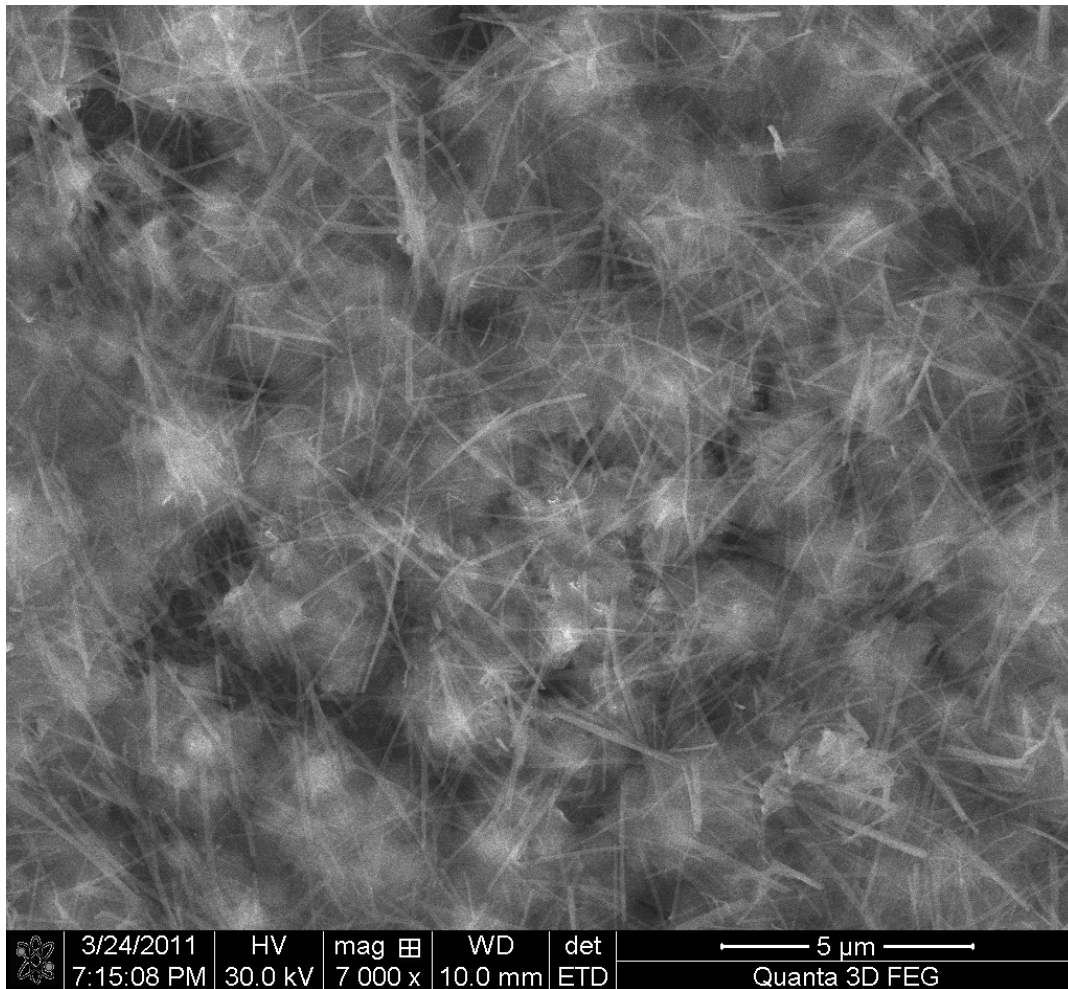


Fig.3(b)

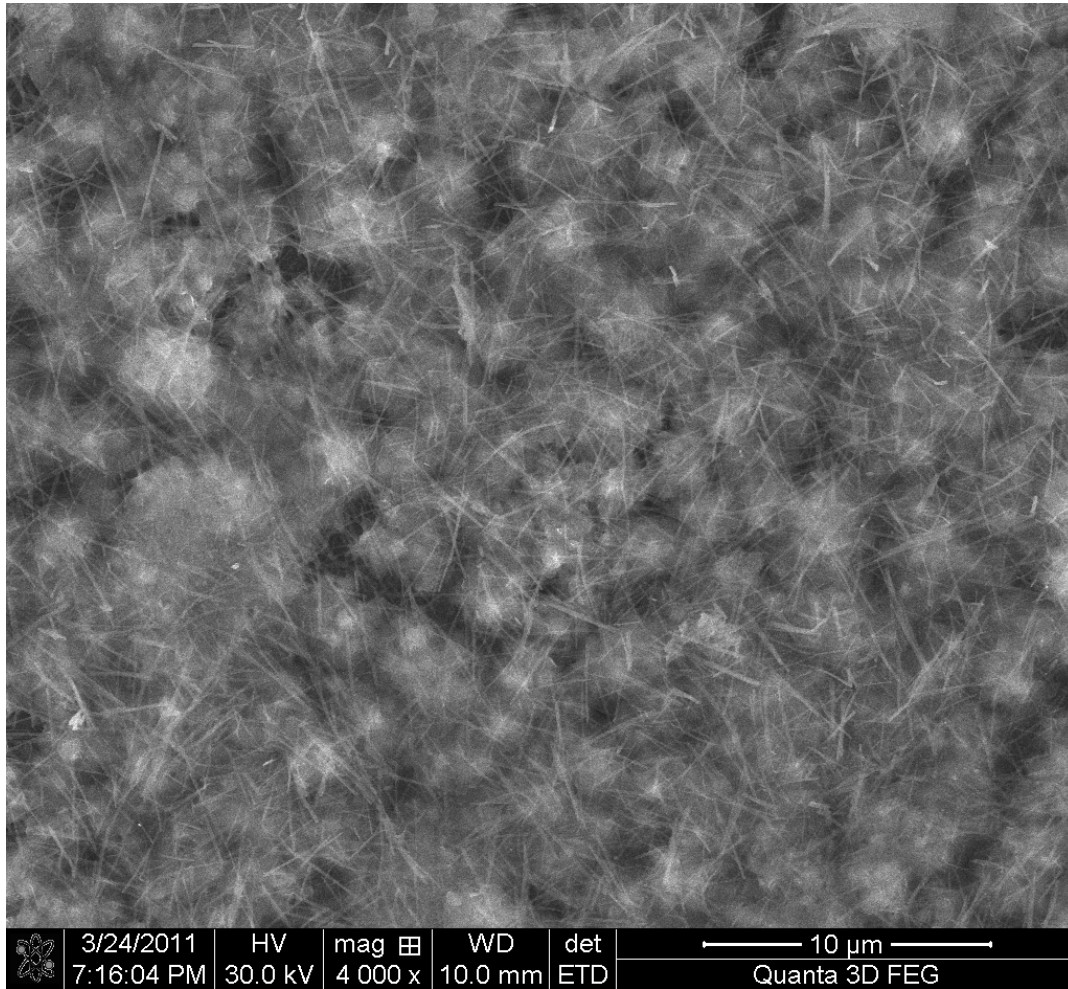
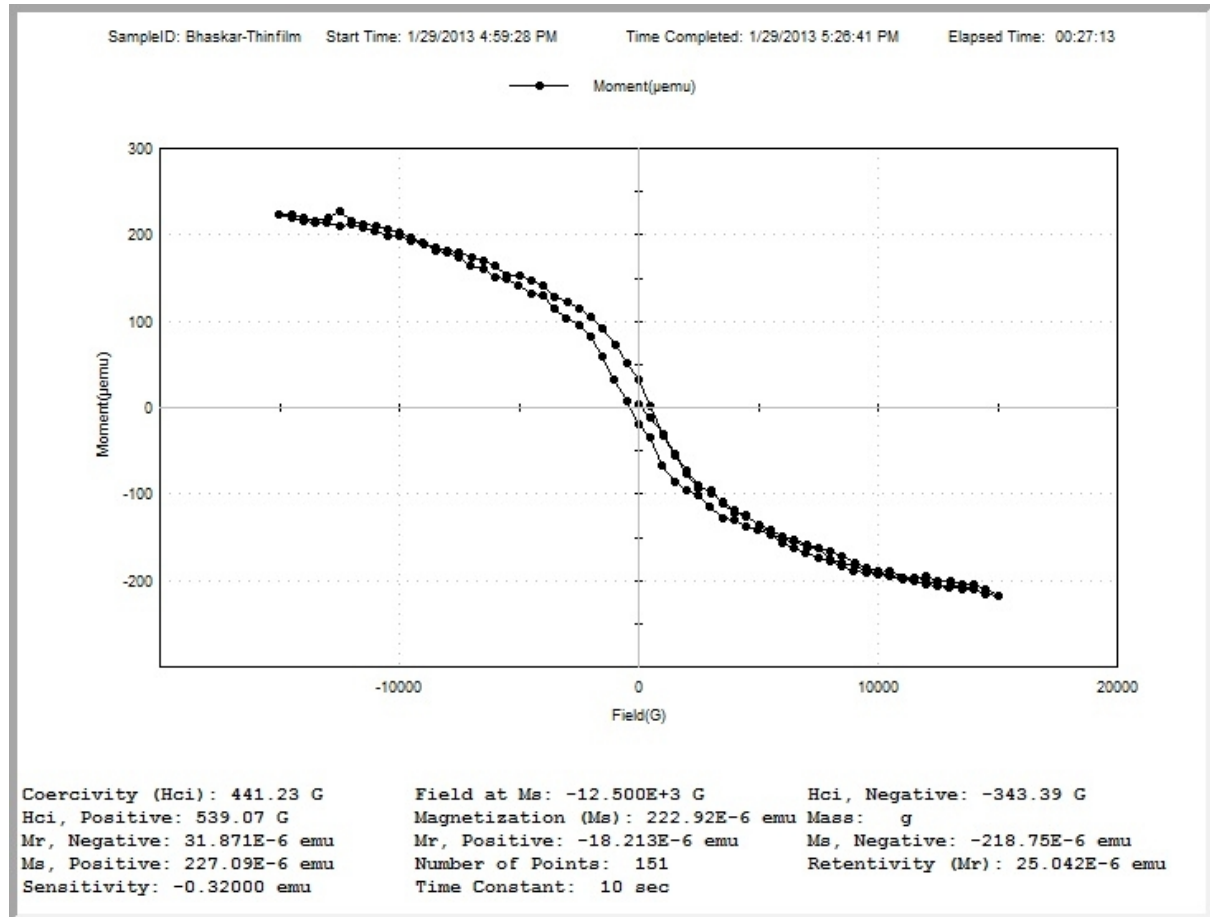


Fig.3(c)

Figure3(a),3(b),3(c) :The SEM images of the prepared ZnO rods

The films deposited on glass further confirms the a- and b-axis orientation with columnar grains running perpendicular to the substrate with average grain size of 120nm (Fig.3(a)). However this study proves ZnO thin films can be prepared by a simple dip coating method for various applications like ITO replacement for photovoltaic panels, inexpensive transistor for disposable electronics and thin film batteries.

VSM:



IV. CONCLUSION

In summary, we have prepared ZnO thin film by simple and inexpensive dipcoating method allowing the large area deposition at low temperature with acceptable film qualities. The films are polycrystalline in nature, possessing hexagonal wurtzite structure. The most prominent peak observed in the film corresponds to (002) plane. Other planes corresponding to (100), (101), (102), (110), (103), etc. are also observed with low relative intensities. The SEM images and EDAX values obtained in the present study indicates the preparation of ZnO rods by a very simple dip coating method yields a film with properties matching the ZnO rods prepared by various other methods. VSM image shows that the as studied ZnO depicts the ferromagnetic property as well which can be exploited for the versatile magnetic applications such as memory devices.

REFERENCES

- [1] N Saito, H Haneda, T Sekiguchi, N Ohashi, I Sakaguchi and K Koumoto, *Adv. Mater.*, **2002**, 14, 418
- [2] M Huang, S Mao, H Feick, H Yan, T Wu, H Kind, E Weber, R Russo and P Yang, *Science*, **2001**, 292, 1897
- [3] J Y Lee, Y S Choi, J H Kim, M O Park and S Im, *Thin Solid Films*, **2002**, 403, 553
- [4] S Liang, H Sheng, Y Liu, Z Hio, Y Lu and H Shen, *J. Cryst. Grow.*, **2001**, 225, 110 [5] M H Koch, P Y Timbrell and R N Lamb, *Semicond Sci Tech*, **1995**, 10, 1523 (1995).
- [5] K Keis, E Magnusson, H Lindstrom, S E Lindquist and A Hagfeldt, *Sol. Energ Mater Sol. Cells*, **2002**, 73, 51 [7] S J Pearton, D P Norton, K Ip, Y W Heo and T Steiner, *Superlatt. Microstr.*, **2003**, 34, 3
- [6] Y Lin, Z Hang, Z Tang, F Yuan, and J Li, *Adv. Mater. Opt. Electron.*, **1999**, 9, 205
- [7] Y C Kong, D P Yu, B Zhang, W Fang, and S Q Feng, *Appl. Phys. Lett.*, **2001**, 78, 4

- [8] Y Cui, Q Wei, H Park and C M Lieber, *Science*, **2001**, 293, 1289
- [9] P M Martin, M S Good, J W Johnston, G J Posakony, L J Bond and S L Crawford *Thin Solid Films*, **2000**, 379, 253
- [10] W I Park, D H Kim, S W Jung and G C Yi *Appl. Phys. Lett.*, **2002**, 80, 4232
- [11] V A L Roy, A B D Jurisic, W K Chan, J Gao, H F Lui and C Surya, *Appl. Phys. Lett.*, **2003**, 83, 141
- [12] B D Yao, Y F Chan, and N Wang, *Appl. Phys. Lett.*, **2002**, 81, 757
- [13] L Vayssieres, K Keis, S E Lindquist and A Hegfeldt, *J. Phys. Chem. B*, **2001**, 105, 3350 [16] X Kong and Y Li, *Chem. Lett.*, **2003**, 32, 838
- [14] Y Li, G W Meng and L D Zhang, *Appl. Phys. Lett.*, **2000**, 76, 2011 [18] M Izaki and T Omi, *Appl. Phys. Lett.*, **1996**, 68, 2439
- [15] Th Pauporte and D Lincot, *Appl. Phys. Lett.*, **1999**, 75, 3817
- [16] B Cao, W Cai, G Duan, Y Li, Q Zhao and D Yu, *Nanotechnology*, **2005**, 16, 2567
- [17] Y W Zhu, H Z Zhang, X C Sun, S Q Feng, J Xu, Q Zhao, B Xiang, R M Wang and D P Yu, *Appl. Phys. Lett.*, **2003**, 83, 144
- [18] M Yan, H T Zhang, E J Widjaja, and R P H Chang, *J. Appl. Phys.*, **2003**, 94, 5240 [23] L Vayssieres, *Adv. Mater.*, **2003**, 15, 464
- [19] G Z Cao, J J Schermer, W J P van Enkevort, W A L M Elst and L J Giling, *J. Appl. Phys.*, **1996**, 79, 1357
- [20] L E Greene, M Law, J Goldberger, F Kim, J C Johnson, Y Zhang, R J Saykally and P Yang, *Angew. Chem. Int. Ed.*, **2003**, 42, 3031
- [21] Chen Xiang Cun et al, *Chin. Phys. B*, **2011**, 20, 9
- [22] Preetam Singh, Ashvani Kumar, Ajay Kaushal, Davinder Kaur, Ashish Pandey and R N Goyal, *Bull. Mater. Sci.*, **2008**, 31, 573–577
- [23] Novel Synthesis and Characterisation of CdS Nanoparticles, M Priya, R S Saravanan and C K Mahadevan, *Energy Procedia*, **2012**, 15, 333–339
- [24] J R Casanova, E A Heredia, C D Bojorge, H R Cãncpa G Kellermann, A F Craievich, *Applied Surface Science*, **2011**, 257, 10045–10051
- [25] N. S. Nirmala Jothi, R. Gunaseelan and P. Sagayaraj, *Archives of Applied Science Research*, **2012**, 4(4), 1698–1704
- [26] Kalpana Rajan. S *, Marimuthu. K. N., Priya. M#. *Archives of Applied Science Research*, 2012, 4 (5):1996-2001