Available online at www.pelagiaresearchlibrary.com

Pelagia Research Library

Pelagia Research Library

Advances in Applied Science Research, 2012, 3 (6):3573-3580

Pelagia Research Library

ISSN: 0976-8610
CODEN (USA): AASRFC

Instrumentation for fabricating an indigenous spin coating apparatus and growth of zinc oxide thin films and their characterizations

P. Sevvanthi, A. Claude*, C. Jayanthi and A. Poiyamozhi

Post Graduate and Research Department of Physics, Government Arts College, Dharmapuri – 636 705
**Post Graduate and Research Department of Physics, Arignar Anna Government Arts College, Villupuram – 605 602 Tamil Nadu, INDIA*

ABSTRACT

Spin coating is an easy and efficient technique to grow good quality thin film crystals and amorphous films suitable for many applications in science in technology namely sensors, filters and solar cells. The engineering and design for the spin coating apparatus was conceived tested and fabricated indigenously in-house inside the laboratory to grow thin film crystals and amorphous films to suit various applications. The rotor consists of an AC motor capable of reaching speeds like 1200 rpm, 2400 rpm and 3600 rpm. A rectangular substrate holder is fabricated on the top of the stub firmly fixed so that not to spin off while reaching the above said high speeds. A transparent lid is fixed with a provision for applying the liquefied charge periodically as droplets onto the substrate. A spill container cum arrestor is fabricated around the spinning platform in order to reduce the splashing and wasting of the charge. The charge is taken in the form of the solution with an optimal texture and super saturation so that the long range order is maintained else there is scope of accumulation and multiple nucleation which will prevent the film from a smooth formation. Homogeneous and Heterogeneous combinations of single layered and multiple layered thin films are realised after effecting a coating with an optimal spin speed. The thin films realised after the process will be subjected to structural, functional and optical characterizations.

Keywords: Spin coating, instrumentation, crystalline, amorphous, homogenous films, heterogenous films

---

INTRODUCTION

A **thin film** is a layer of material ranging from fractions of a nanometer (monolayer) to several micrometers in thickness. Electronic semiconductor devices and optical coatings are the main applications benefiting from thin film formations[1]. A familiar application of thin films is the household mirror, which typically has a thin metal coating on the back of a sheet of glass to form a reflective interface. The process of silvering was once commonly used to produce mirrors. A very thin film coating (less than a nano metre thick) is used to produce two-way mirrors. The performance of optical coatings (e.g. antireflective, or AR, coatings) are typically enhanced when the thin film coating consists of multiple layers having varying thicknesses and refractive indices. Similarly, a periodic structure of alternating thin films of different materials may collectively form a so-called super lattice which exploits the phenomenon of quantum confinement by restricting electronic phenomena to two-dimensions [2]. Work is being done with ferromagnetic and ferroelectric thin films for use as computer memory. It is also being applied to pharmaceuticals, via thin film drug delivery. Thin-films are used to produce thin-film batteries. Thin film

application can also be adopted on dye-sensitized solar cell. Ceramic thin films are also widely of use nowadays. The relatively high hardness and inertness of ceramic materials make this type of thin coating of interest for protection of substrate materials against corrosion, oxidation and wear. In particular, the use of such coatings on cutting tools can extend the life of these items by several orders of magnitude [3]. Research is being done on a new class of thin film inorganic oxide materials, called amorphous heavy-metal cation multi-component oxides, which could be used to make transparent transistors that are inexpensive, stable, and environmentally benign [4].

The act of applying a thin film to a surface is thin-film deposition. This is a technique for depositing a thin film of the selected material onto a substrate or onto previously deposited layers. "Thin" is a relative term, but most deposition techniques control layer thickness within a few tens of nanometres. Molecular beam epitaxy allows a single layer of atoms to be deposited at a time. It is useful in the manufacture of optics (for reflective, anti-reflective coatings or self-cleaning glass, for instance), electronics (layers of insulators, semiconductors, and conductors form integrated circuits), packaging (i.e., aluminium-coated PET film), and in contemporary art [5]. Similar processes are sometimes used where thickness is not important: for instance, the purification of copper by electroplating, and the deposition of silicon and enriched uranium by a CVD-like process after gas-phase processing. Deposition techniques fall into two broad categories, depending on whether the process is primarily chemical or physical.

This paper aims at producing ZnO coatings on a variety of transparent glass and opaque metal substrates viz., Glass, Aluminum and Zinc Substrates respectively. Various compositions of ZnO coatings [6] by varying coating times using Zinc Nitrate ($ZnNO_3$) as starting materials were tried. Further the idea of deposition upon metal substrates aims at totally weeding out the necessity of ITO (Indium Tin Oxide) coatings which is costly for procurement and tedious affair when it is coated inside the laboratory.

1. INSTRUMENTATION FOR SPIN COATING

For this experiment the machine a “spin coater”, whose idea is conceived, designed and fabricated indigenously in our laboratory. The rotor consists of an AC motor capable of reaching speeds like 1800rpm, 2400rpm and 3600rpm. A rectangular substrate holder is fabricated on the top of the stub firmly fixed so that not to spin off while reaching the above said high speeds. A transparent lid is fixed with a provision for applying the liquefied charge periodically as droplets on to the substrate [7]. A spill container cum arrestor is fabricated around the spinning platform in order to reduce the splashing and wasting of the charge. The charge is taken in the form of the solution with an optimal texture and super saturation so that the long range order is maintained else there is scope of accumulation and multiple nucleation which will prevent the film from a smooth formation.

Fig. 1: Spin Coater with spill arrestor

Homogeneous and heterogeneous combinations of single layered and multiple layered thin films are realized after effecting a coating with an optical spin speed [8]. The thin films realized after the process will be subjected to

structural functional and optical characterization. There are several major factors affecting the coating process among these are spin speed, acceleration, spin time, and exhaust.

2. SPIN COATING OF ZINC OXIDE THIN FILMS

ZnO thin film is one of the II-VI compound semiconductors and is composed of hexagonal wurtzite crystal structure. ZnO thin film presents exciting investigations and results for optical, acoustical and electrical properties which meets various applications in the fields of electronics, optoelectronics and sensors [9]. ZnO thin film is applied to the transparent conductive films and the solar cell windows because of the high optical transmittance in the visible region studied by the application of ZnO thin film to the surface acoustic wave (SAW) device and Film Bulk Acoustic Resonator (FBAR) filter being made, because of its excellent piezoelectric properties. In this study, Zinc Oxide is spin coated on glass substrates and also on metal substrates using Zinc Nitrate ($ZnNO_3$) as precursor optimally in solvent form.

MATERIALS AND METHODS

ZnO thin film is one of the II-VI compound semiconductors and is composed of hexagonal wurtzite crystal structure. ZnO thin film presents exciting investigations and results for optical, acoustical and electrical properties which meets various applications in the fields of electronics, optoelectronics and sensors [10]. ZnO thin film is applied to the transparent conductive films and used as solar cell window materials because of the high optical transmittance in the visible region studied by the application of ZnO thin film to the surface acoustic wave (SAW) device and Film Bulk Acoustic Resonator (FBAR) filter being made, because of its excellent piezoelectric properties.

The ZnO thin film is prepared using various methods such as spray paralysis sputtering, sol-gel spin coating, pulsed laser deposition (PLD), chemical vapor deposition(CVD) and various other methods. In spite of few studies regarding to the spin coating method, it naturally has some merits, such as easy method has control of chemical components and fabrication of thin film at a low cost. Zinc Nitrate is taken in optimal proportions and dissolved in double distilled de-ionised water and applied as drops on the spin coater to make uniform coating. The film thickness however depends on the evaporation rate [11] of the solvent after spin coating application. We distinguish three possible cases.

1. The solvent is not evaporating this means, the film thickness (d) depends only on the rotational speed (w) and spinning time(t)

$d \alpha w^{-1} t^{-1/2}$

2. The solvent evaporates with a constant rate.

$d \alpha w^{-2/3}$

3. Solvent evaporation varies with the square root of the angular velocity.

$d \alpha w^{-1/2}$

In the spin coating process the interactions between substrate and solution layer are stronger than the interaction between solution surface layer and air. During the spin coating process the solvent evaporates, this leads to an increasing concentration and therefore increasing viscosity, which effects the pattern of formation. The film thickness is depends on the viscosity and concentration of the solution of Zinc Nitrate used [12]. The more concentrated the solution is the thicker gets the film. The reverse holds for the dependency of film thickness on angular velocity.

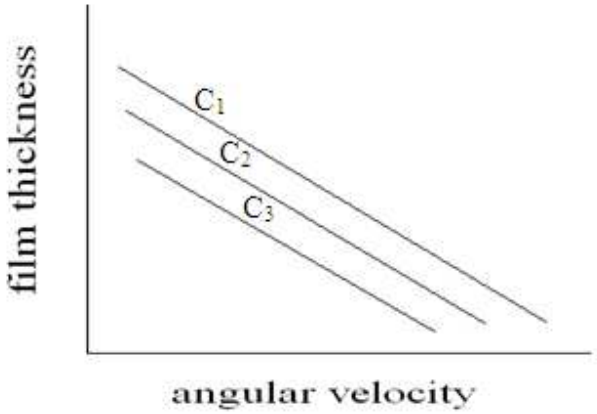

Fig. 2: Film thickness against angular velocity by varying concentrations of the solution.

3. X-Ray Diffraction of ZnO thin film

The crystal structure and orientation of the ZnO thin films were investigated by X-ray diffraction (XRD) patterns. The XRD spectra for ZnO thin films shown in figure 3 below.

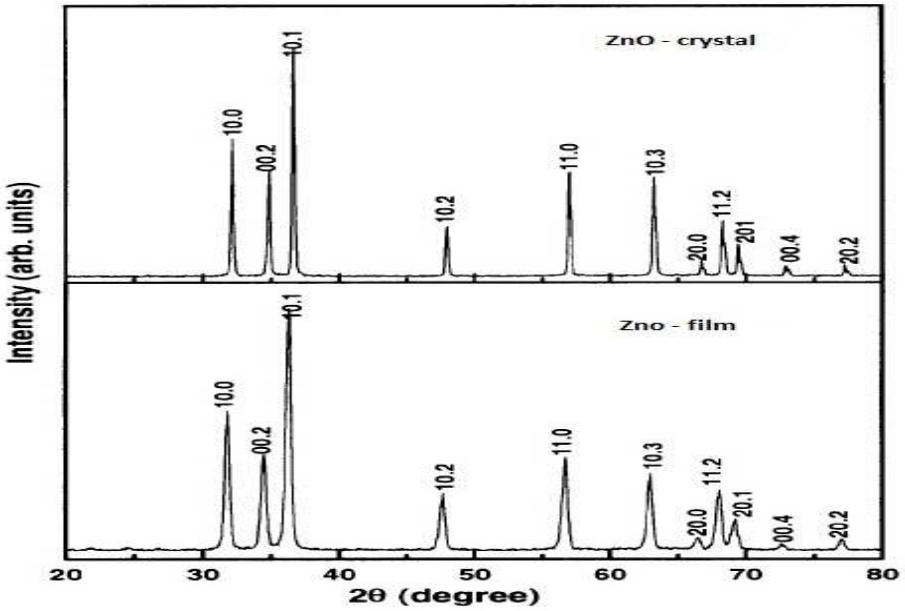

Fig.3: Comparative powder XRD spectrum

Powder X-Ray diffraction was carried out using a Rich-Siefert Diffractogram where the crushed and powdered sample was analysed using X-rays from a CuKα (λ=1.54059 Å) radiation) radiation. The observed peaks were compared with ICDD file no. 35-1482 and hexagonal *ZnO* (wurtzite, *JCPDS* 36-1451. The lattice constants for hexagonal ZnO film are reported in JCPDS standard data *a*=3.24982 Å and *c*=5.20661 Å [13]. The analytical method [14] was used to calculate lattice constants *a* and *c* for ZnO film. The calculated values of *a* and *c* were found to be 3.21907 Å and 5.15760 Å, respectively. These calculated values are in agreement with JCPDS data.

XRD diffraction peaks belonging to (100), (002)and (101) planes were observed in all the ZnO films compared to powder diffraction data of zincite structure. The XRD patterns of all the samples indicated enhanced intensities for the peaks corresponding to(002)plane, indicating preferential orientation along the c-axis The XRD spectra indicate that the films are of polycrystalline structure. The grain size of crystallites was found to be in the range of 25-32 nm.

The values of the optical band gap and Urbach energy (energy associated with the nature of coatings formed) changes with chuck rotation rate.

Table 1: Indexing table for ZnO peaks from XRD

(h k l)	2θ	d(Å)	I/Io	TC(hkl)
(1 0 0)	32.080	2.7878	1.4	0.0788
(0 0 2)	34.760	2.5788	100	5.6285
(1 0 1)	36.580	2.4546	3.0	0.1689
(1 0 2)	47.879	1.8984	0.5	0.0281
(1 1 0)	56.919	1.6164	0.4	0.0225
(1 0 3)	63.159	1.4709	1.3	0.0732

Table 2: Comparative available and reported values of XRD

d_{XRD} (A^0)	d_{JCPDS} (A^0)	(*hkl*)
2.80	2.82	(100)
2.63	2.60	(002)
2.51	2.48	(101)
1.92	1.91	(102)
1.61	1.63	(110)
1.39	1.38	(112)

4. Optical properties of the ZnO thin films

The optical transmittance and absorption co-efficient spectra of the thin films in the UV-Visible wavelength range are present below. A PE Lambda UV-Vis spectrophotometer was engaged to take the spectrum. Some sharp absorption peaks were seen at 300nm, 327nm, 381nm respectively in the UV region. The thin films were found to have around 90% transmission which depicts the quality of formation from spin coatings.

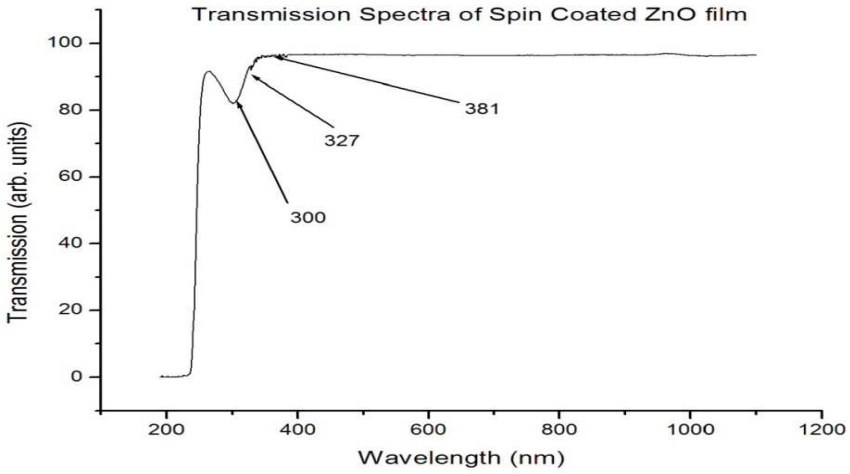

Fig. 4: Transmission spectra of ZnO thin film

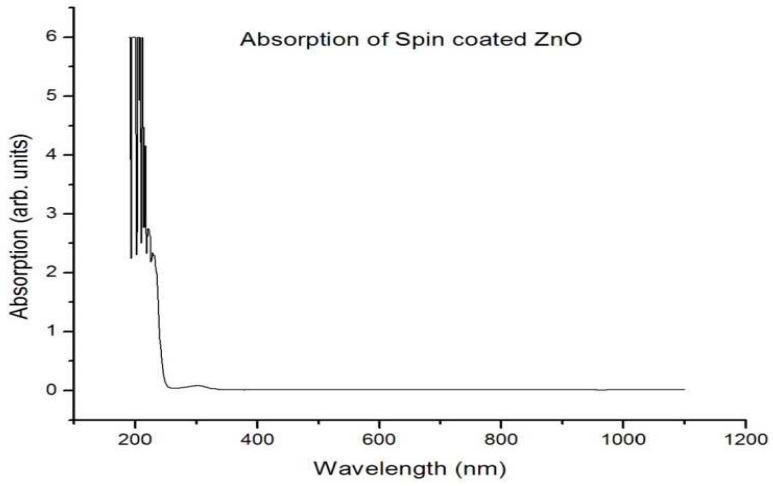

Fig. 5: Absorption spectra of ZnO thin film

A shift of the initial absorption edge was observed and this is associated with Burstein-Moss effect. In the visible region, all the films are seen to be highly transparent having minimal to very minimal absorption.

5. The I-V characteristics of the thin film

The measured dark and illuminated I-V characteristics are shown in figure.

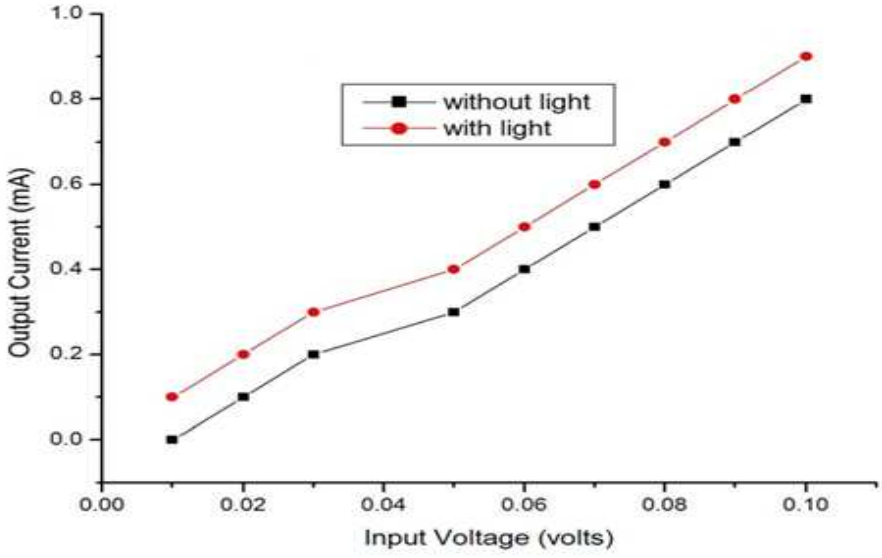

Fig. 6: I-V Characteristics of ZnO thin films

Ohmic behaviors and non-linear behavior in the I-V curves were observed in the ZnO thin films in dark and under light illumination, respectively. The current at a given voltage for the films under light illumination is higher than that under dark conditions. This indicates that the light illumination increases the production of electron hole pairs.

The I-V characteristics of the films in dark and under illumination shows that the spin coated ZnO thin films are sensitive to light. It is thought that because of these properties, ZnO thin films can be used as a base solar cell

material and also as a window material in photovoltaic applications. The effect of the light on the films shows that the obtained ZnO thin films can be used as a photovoltaic material owing to its photoconductive nature.

6. FTIR spectrum of ZnO thin films

The FTIR spectra was taken using the same PE-Lambda spectrophotometer between 400-4000nm range. Fig. 7: shows the FT-IR spectra of ZnO thin film, absorption bands near 3411 cm^{-1} which represent O-H stretching mode, those at 2911 cm^{-1} are C-H bending mode, and 1409-1605 cm^{-1} are the C=O stretching mode. As the temperature increases, the organic band at 1409-1605 cm^{-1} is removed, but the bands arising from the absorption of atmospheric CO2 on the metallic cations at 2303 cm^{-1} and bonding between Zn-O (611cm^{-1}, 735 cm^{-1}) are clearly represented.

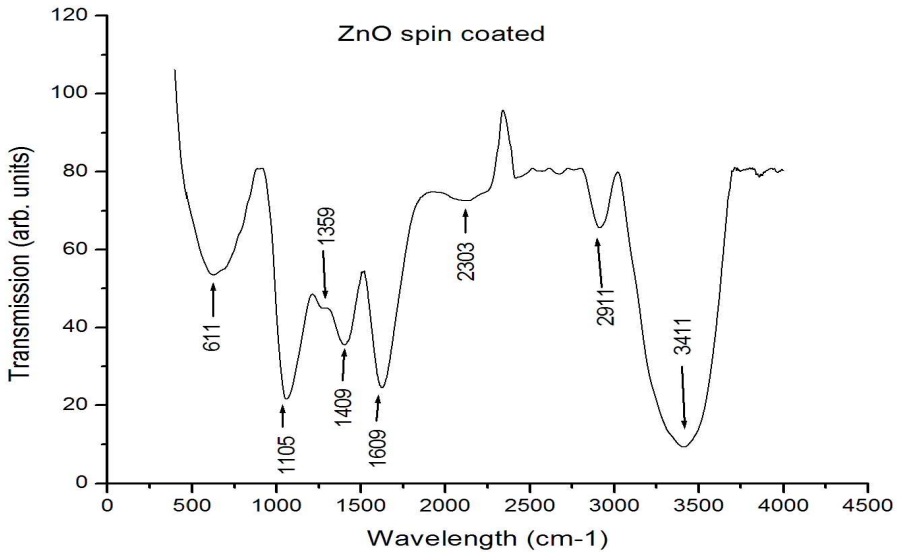

Fig.7: FTIR Spectrum of ZnO thin film

CONCLUSION

A versatile spin coating apparatus was indigenously built using natively available materials. A coating of Zinc Oxide which is a promising Solar Cell material [15] is grown as a thin film on glass substrate [16]. The grown thin films were confirmed for their structural parameters using XRD analysis. The I-V response of the grown films of Zinc Oxide confirms photoconductive behavior [17-19]. FTIR analysis indicates the essential vibrations [20-22] which confirms the bonds in Zinc Oxide.

Acknowledgement

The author (AC) records his gratitude for various useful and fruitful interactions with Dr G. Bagavannarayana, Dr. N. Vijayan Scientists at National Physical Laboratory, New Delhi, Dr. R. Gopalakrishnan, Assistant Professor at Physics Department, Anna University: Chennai and Prof. P. Ramasamy, Dean Research, SSNCE and Mr. Vincent of ACIC at St. Josephs College, Trichy. The Author is also thankful to his past Principal and Prof. A. Poiyamozhi, Head, PG & Research Department of Physics, Govt. Arts College, Dharmapuri, and his present Principal Dr. Rangarajan, and Prof. R. Muthulakshmi, Head, PG and Research Department of Physics, Arignar Anna Government Arts College, Villupuram and all his past and present teaching colleagues for their kindness and support.

REFERENCES

[1] L. D. Landau, B. G. Levich, *Acta Physiochim*, **1942,** 17, 42-54
[2] I. Strawbridge, P. F. James, *J. Non-Cryst. Solids*,**1986,** 82, 366 - 372
[3] C. J. Brinker, A. J. Hurd, K. J. Ward, *Ultrastructure Processing of Advanced Ceramics,* eds. J. D. Mackenzie and D. R. Ulrich, Wiley, New York , **1988**, 223

[4] H. Schröder, *Physics of Thin Films*, Academic Press, New York - London, vol. 5, **1969**, 87 – 141.
[5] N. J. Arfsten, A. Eberle, J. Otto, A. Reich, *J. Sol-Gel Science and Technology*, **1997,** 8, 1099-1104
[6] D. Meyerhofer, *J. Appl. Phys.*, **1978,** 49, 3993 – 3997.
[7] H. G. Floch, F. Belleville, J.-J. Priotton, *Am. Ceram. Soc. Bull*., **1995,** 74, 60 – 63.
[8] A. Atkinson, J. Doorbar, A. Hudd, D. L. Segal, P. J. White, J. Sol-Gel Science and Technology, **1997,** 8, 1093-1097.
[9] O. Yamamoto, T. Sasamoto, M. Inagaki, *J. Mater. Res.*, **1992,** 7, 2488.
[10] A. Maddalena, R. Del Machio, S. Diré, A. Raccanelli, *J. Non-Cryst. Solids*,**1990,** 121, 365.
[11] J. P. Chatelon, C. Terrier, E. Bernstein, R. Berjoan, J. A. Roger, *Thin Solid Films*, **1994,** 247, 162.
[12] C. Terrier, J. P. Chatelon, R. Berjoan, J. A. Roger, *Thin Solid Films*, **1995,** 263, 37.
[13] A. Agrawal, J. P. Cronin, R. Zhang, *Solar Energy Materials and Solar Cells*, **1993,** 31, 9.
[14] P. Judeinstein, J. Livage, A. Zarndiansky, R. Rose, *Solid State Ionics*, **1988**, 28-30, 1722-43.
[15] M. Aegerter, *Structure and Bonding*, **1996,** 85, 149 – 194.
[16] A. Kalleder, M. Mennig, H. Schmidt, *J. Non-Cryst. Sol.*, **1997,** 218, 399 – 402.
[17] M. Mennig, M. Schmitt, U. Becker, G. Jung und H. Schmidt, *SPIE 2288: Sol-Gel Optics III*, Editor: J. D. Mackenzie. SPIE, Bellingham/ Washington, **1994**, 130 - 139.
[18] D. S. Bhavsar, *Advances in Applied Science Research*, **2012**, 3(3), 1250-1254
[19] N. A. Okereke and A. J. Ekpunobi, *Advances in Applied Science Research*, **2012**, 3 (3), 1244-1249
[20] R S Meshram, B M Suryavanshi and R M Thombre, *Advances in Applied Science Research*, **2012**, 3 (3), 1563-1571.
[21] D. K. Sawant and D. S. Bhavsar, *Der Chemica Sinica*, **2011**, 2 (4), 211-218.
[22] N. S. Shinde, S. S. Khot, B. P. Ladgaonkar, B. B. Kale, S. Apte, P. M. Tamhankar and S. C. Watawe, *Der Chemica Sinica*, **2011**, 2(4), 252-261.