



ROOM TEMPERATURE ELECTRO-SYNTHESIS OF NANOCRYSTALLINE NICKEL DOPED ZINC OXIDE THIN FILMS.

N.P. Tendolkar

Department of Physics, Athalye, Sapre and Pitre College, Devrukh, Dist: Ratnagiri, Maharashtra.

M. R. Kale*

Department of Physics, Athalye, Sapre and Pitre College, Devrukh, Dist: Ratnagiri, Maharashtra. *Corresponding author

ABSTRACT

Zinc oxide (ZnO) has wide range of technological applications as transparent conducting electrodes in solar cells, flat panel displays, surface acoustic wave devices, and sensors. Moreover, it is widely heralded that spintronic devices would provide advantages over their conventional counterparts, such as non-volatility, higher speed, lower power consumption, and higher integration density. Electrodeposition is one of the chemical methods for preparation of thin films. It is simple, convenient, less expensive among the various physical and chemical methods. One can deposit binary and ternary metal chalcogenides, oxides at room temperature by using this method.

In this work single step electro-synthesis of nickel doped zinc oxide thin films from alkaline bath (which avoids anodization step for an incorporation oxygen species into deposit) has been carried out at room temperature. Small heat treatment converts these to the oxide phase. The X-ray diffraction studies confirmed the formation of nickel doped zinc oxide thin films with wurtzite crystal structure. The standard and observed d values are comparable.

KEYWORDS : Electrosynthesis, Nickel- Zinc oxide, XRD.

INTRODUCTION

The Semiconductor ZnO has gained Substantial interest in the research community in part because of its wide band gap energy (3.3eV), eco-friendly and transparency etc. Dilutemagnetic semiconductors have attracted a great deal of attention in the past few years as enabling materials in the emerging field of spintronics¹. DMS are semiconductor solid solutions where a small percentage of cations are replaced by magnetic impurities [1-5]. DMS which combine the two interesting properties magnetic and semiconducting are considered as an ideal system for spintronic multi-functional properties of ZnO make it suitable for applications in electronic and optoelectronic devices. Due to its versatility, ZnO has drawn considerable attention and has been prepared and investigated in various physical forms such as single crystals, sintered/ceramic pellets, thick films, thin films and nanostructures etc. Among different physical forms, the thin films of ZnO find a multitude of immensely important applications in electronic and optoelectronic devices such as photo thermal conversion systems, transparent conductors, gas sensors for toxic and combustible gases and heat mirrors among many others. Thin films form the basis for many electronic components and are of particular interest for fabrication of large area arrays. Thus most of the device applications require ZnO in polycrystalline thin film form [6-10]. Ni doped ZnO has been observed as an important candidate in the field of DMSs [11]. A very few studies has been carried out on NiZnO system due to the phase segregation of ZnO and NiO. This happens due the large driving force of Ni-O bond as compared to Zn-O bond [12].

Electrically ZnO is an n-type degenerate semiconductor with huge dielectric constant and exhibits activated conduction behaviour [13]. ZnO possess hexagonal wurtzite structure where there is a tetrahedral coordination of Zn atoms with four oxygen atoms. The Zn s - electrons hybridize with the oxygen p-electrons. Introducing impurities by an appropriate method in ZnO not only provides an insight into the study of its electronic properties, but also provides a great interest in studying its optical properties. The isovalent nature of ZnO and transition metal ions (TMI) has made it possible to dope ZnO with Al [14], Ga [5-7], Co, Ni [11], Cd [15] and Mg [16]. There has been a great deal of attention on search for magnetism in transition metal (TM) ion doped ZnO [17-23] which will make it an important candidate for dilute magnetic Semiconductor (DMS) spintronic applications.

This work presents single-step electrodeposition of nickel-zinc

ferrite thin films at room temperature from alkaline solutions. These ferrite films synthesized are employed for the structural elucidation and morphological studies. It is perceived that there is no formation of byproduct species and material conservation, revealing the method importance in synthesizing single-stroke ferrite films at ambient temperature.

Experimental

For the deposition of nickel zinc oxide thin films standard three-electrode system was used. Nickel sulphate and zinc sulphate solutions were used as source for nickel and zinc metal ions, respectively. The 0.1 M citric acid was used as complexing agent whereas 1 N NaOH was used to make bath alkaline. Preparation of nickel zinc oxide thin films was carried out at room temperature from unstirred electrolyte. Solutions of nickel and zinc sulphates were mixed in various proportions to optimize the bath composition. The dopant material i.e Nickel is mixed with solution of zinc sulphate in various appropriate proportion like 1%, 2% etc. total quantity of electrolytic bath was fix (20 ml). By varying different values of currents, and deposition time was optimized. Various preparative parameters were optimized to electrodeposits uniform and adherent nickel doped Zinc oxide thin films, and are summarized in Table 1.

Table 1 Optimized preparative parameters for nickel doped zinc oxide films

Preparative parameters	Varied range	Optimized parameters
Deposition current	0.01 to 0.09 μ A	0.05 μ A
Deposition time (min)	5 to 30	25

Blackish colored as-deposited nickel-zinc oxide thin films were annealed for 1hour at 773K temperature and furnace cooled. The crystallinity of nickel-zinc oxide thin films (annealed) were studied by X-ray diffraction carried out with Philips PW-3710 X-ray diffractometers.

RESULT AND DISCUSSION

Nickel zinc oxide film thickness

For the measurement of thickness of nickel zinc oxide film, a gravimetric weight difference method was used. Fig.1 shows plot of film thickness against deposition time for nickel zinc oxide thin film deposited at applied constant 0.05 A. From Fig.1 it is observed that, film thickness was increased with increase in current and attained maximum value of 0.72 μ m for 25 min time period.

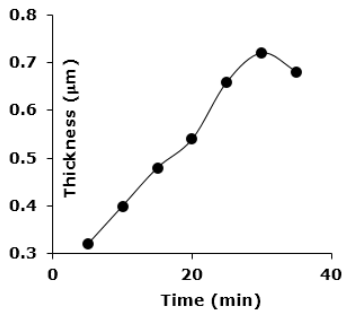


Fig 1 A plot of thickness against deposition time for nickel doped zinc oxide thin films.

XRD Studies

For the structural identification of nickel zinc oxide thin film, X-ray diffraction technique was used.

The XRD patterns of the 1 wt % Ni doped, 2 wt % Ni doped and 3 wt % Ni doped ZnO are shown in Fig.2. a, b and c respectively. The sharp and intense peaks indicate that the samples are highly crystalline and ZnO nanocrystalline films have polycrystalline structure. The XRD peaks for (100), (002), (101), (102), (110), (103) and (112) planes indicates the formation of phase pure wurtzite structure of ZnO. The crystallite size of Ni-doped ZnO is calculated using Scherrer's formula [3.4] and given in Table 6.8. It is seen from the figure 2, for all the samples dominant peaks are (100), (002) and (101). For 1 wt% Ni doped ZnO the full width half maximum (β) of the above dominant peaks are 0.3097, 0.3313 and 0.3261, while for 2% Ni doping the (β) of the peaks become 0.3973, 0.3641 and 0.3619. However, that the intensities of diffraction peaks decline as the Ni²⁺ ion concentration increases, i.e. the nickel doping within the films causes the ZnO crystallinity to deteriorate. Since the intensity of diffraction peaks becomes weaker and the half-peak width becomes wider with the increase of dopant concentration, the Ni²⁺ ions inhibit the aggregation of ZnO nanocrystals [Nina V et al., 2011] and affect the crystallization of ZnO. For further increase of nickel that is 3 wt% Ni doped ZnO the (β) of the peaks become 0.2769, 0.2629 and 0.2930 and the crystallite size increases. (002) peak is found to be dominant for all Ni doped ZnO films for lower dopant concentration. For 3% dopant concentration the grains have preferential growth along (101) plane by making the corresponding peak with the higher intensity.

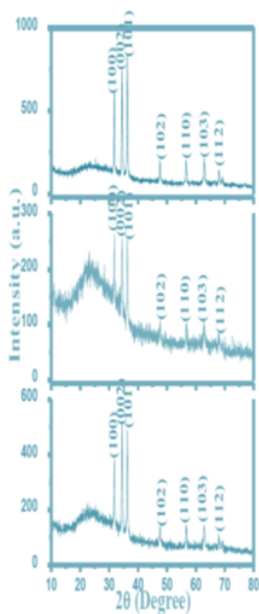


Fig.2.(a, b and c) XRD patterns for annealed Nickel doped Zinc oxide thin films.

Remarkable conclusions

In a single step electrodeposition, nanocrystalline Nickel zinc oxide thin film formation was made possible at room temperature. Due to an alkaline bath, incorporation of oxygen in solid film was possible and resulted into oxide thin film formation. Generally oxide thin films can be prepared at high temperature and with the use of sophisticated instrumentation. But by using this single step electrosynthesis method, oxide thin film formation at room temperature is possible, which avoids many environmental hazardous events, as this method is eco-friendly and convenient too. Doping of ZnO with Nickel has been achieved. XRD of all the films contain (100), (002), (101), (102), (110), (103) and (112) peaks, which indicate that are all polycrystalline in nature.

ACKNOWLEDGEMENT

This work is supported by minor research project sanctioned by University of Mumbai, Maharashtra. One of the author (NPT) wish to thank university of Mumbai, Maharashtra.

REFERENCES

1. Aricò, A. S., P. Bruce, et al. *Nature Materials*(4):366-377(2005).
2. Chu, A. and P. Braatz *Journal of Power Sources* 112(1):236-246(2002).
3. L.L. Zhang, X.S. Zhao, *Chem. Soc. Rev.*, 38 (2009) 2520.
4. A. Janes, H. Kuriig, E. Lust, *Carbon*, 45 (2007) 1226.
5. S.W. Hwang, S.H. Hyun, *J. Nano-crystalline Solids*, 347 (2004) 238.
6. X. Zhao, H. Tian, M. Zhu, K. Tian, J.J. Wang, F. Kang, R.A. Outlaw, *J. Power Sources*, 194 (2009) 1208.
7. E. Frackowiak, K. Jurewicz, K. Szostak, S. Delpeux, F. Beguin, *Fuel Process. Technol.*, 77 (2002) 213.
8. J. Yan, T. Wei, W. Qiao, Z. Fan, L. Zhang, T. Li, Q. Zhao, *Electrochem. Commun.*, 12 (2010) 1279.
9. T. Liu, W.G. Pell, B.E. Conway, *Electrochim. Acta*, 42 (1997) 3541.
10. L. Chen, L.J. Sun, F. Luan, Y. Liang, Y. Li, X.X. Liu, *J. Power Sources*, 195 (2010) 3742.
11. J.B. Cui, U.J. Gibson, *Appl. Phys. Lett.* 87, 133108 (2005).
12. J. Mohapatra, D.K. Mishra, S.K. Kamilla, V.R.R. Medicherla, D.M. Phase, V. Berma, S.K. Singh, *phys. status solidi b* 248, 1352 (2011).
13. S. Singh, N. Rama, K. Sethupathi, M.S.R. Rao, *J. Appl. Phys.* 103, 07D108 (2008).
14. A. Seguro, J.A. Sans, D. Errandonea, D. Martinez-Garcia, V. Fages, *Appl. Phys. Lett.* 88, 011910 (2006).
15. T. Makino, Y. Segawa, S. Yoshida, A. Tsukazaki, A. Ohtomo, M. Kawasaki, *Appl. Phys. Lett.* 85, 759 (2004).
16. J. Zhong, S. Muthukumar, Y. Chen, Y. Lu, H.M. Ng, W. Jiang, E.L. Garfunkel, *Appl. Phys. Lett.* 83, 3401 (2003).
17. C. Xu, M. Kim, J. Chun, D. Kim, *Appl. Phys. Lett.* 86, 133107 (2005).
18. J.B. Cui, U.J. Gibson, *Appl. Phys. Lett.* 87, 133108 (2005).
19. Q.H. Li, Q. Wan, Y.G. Wang, T.H. Wang, *Appl. Phys. Lett.* 86, 263101 (2005).
20. N.H. Hong, J. Sakai, A. Hassini, *J. Phys: Condens. Mat.* 17, 199 (2005).
21. T. Wakano, N. Fujimura, Y. Morinaga, N. Abe, A. Ashida, T. Ito, *Physica E* 10, 260 (2001).
22. W. Jung, S.J. An, G.C. Yi, C.U. Jung, S.I. Lee, S. Cho, *Appl. Phys. Lett.* 80, 4561 (2002).
23. B. Srinivasa Rao, B. Rajesh Kumar, G. Venkata Chalapati, V. Rajagopal Reddy, T. Subba Rao, *J. Nano- Electron. Phys.* 3, No 1, 620 (2011).