

Optical and Electrical Properties of Nanostructured Nio Thin Films Deposited By Chemical Spray Technique

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ABSTRACT

A simple and inexpensive spray pyrolysis technique (SPT) was employed to deposit nickel oxide (NiO) thin films on to glass substrates at 573 K using nickel chloride as starting solution. The optical and electrical properties were studied using optical absorption, electrical resistivity and thermoelectric power (TEP) techniques. The optical characterization shows that the band gap of the spray deposited NiO thin film is 3.3eV.The electrical resistivity of NiO thin film is of the order of $10^6 \ \Omega cm$. The thermo-emf measurement confirms n-type conductivity of NiO thin films.

Keywords: Thin films; Nanostructures; Electrical properties; Optical properties.

1. Introduction

Metal oxides can adopt a large variety of structural geometries with an electronic structure that may exhibit metallic, semiconductor, or insulator characteristics, endowing them with diverse chemical and physical properties. Therefore, metal oxides are the most important functional materials used for chemical and biological sensing and transduction. Moreover, their unique and tunable physical properties have made themselves excellent candidates for electronic and optoelectronic applications. Nanostructured metal oxides have been actively studied due to both scientific interests and potential applications [1,2].

NiO is an important anti ferromagnetic semiconductor with excellent properties such as gas-sensing, catalytic and electrochemical properties, and has been studied widely for applications in solid-state sensors, electro chromic devices and heterogeneous catalysts as well as lithium batteries. The nickel oxide thin films have been prepared using various techniques including thermal evaporation [3], spray pyrolysis [4], chemical vapor deposition [5], electrochemical deposition [6], sol-gel [7,8], sputtering [9-11], chemical solution deposition [12-16], etc. Among these, chemical spray deposition techniques is an advantageous technique due to its low cost, low-temperature operating condition and freedom to deposit materials on a variety of substances. Varkey and Fort [14] deposited nickel oxide thin films using nickel sulfate and ammonia solution over the temperature range 330 - 350 K. Pramanik and Bhattacharya [12] prepared nickel oxide thin films from an aqueous solution composed of nickel sulfate, potassium per sulfate, and ammonia at room





temperature. Han et al. [15] studied growth mechanism of nickel oxide thin films. Banerjee et al. [16] obtained hexagonal mesoporous nickel oxide using dodecyl sulfate as a surfactant and urea as a hydrolyzing agent.

In the present work, chemical spray pyrolysis method was utilized for the deposition of nanocrystalline NiOthin films onto glass substrates at 573 K. The various deposition parameters were optimized to get good quality NiO thin films. The optical and electrical properties were studied by using optical absorption, electrical resistivity and thermo-emf measurement techniques.

2. Experimental Details

Chemical Spray pyrolysis is a versatile and effective technique to deposit wide variety of nanostructured metal oxide, metal chalcogenides and selenides thin filmsAll the compounds used for preparation of NiO films were brought into their ionic form by using fresh doubly distilled water. To obtain NiO thin film nickel chloride solution of 0.15M was used. Before deposition the substrates were boiled in the concentrate chromic acid (0.5M) for 1 hour and then kept in it for next 48 hours. The substrates were then washed with double distilled water. The spray deposition method involves the decomposition of an aqueous solution of nickel chloride. The 0.15M nickel chloride solution was sprayed using compressed air as a carrier gas onto hot glass substrates kept at 573 ±5K temperature. Several trials were conducted to optimize the different deposition parameters such as substrate temperature, spray rate, concentrations of cationic and anionic sourcesetc. The optimized deposition temperature was found to be \approx 573 K. The films deposited below this temperature werediscontinuous and less adhesive. The optimized spray rate was found to be 6 mL min-1. The films deposited above this spray rate are discontinuous with cracks which may be due to incomplete thermal decomposition. However, films deposited at low spray rate are discontinuous due to insufficient quantity of sprayed solution. The average thickness of the as deposited NiOthin film was measured by the gravimetric method. The optical characteristics were studied using UV-VIS-NIR spectrophotometer (Hitachi-330), to find band gap energy of NiO thin films. The dc two-point probe method of dark electrical resistivity was used to study the variation of resistivity with temperature.

3. Results and discussion

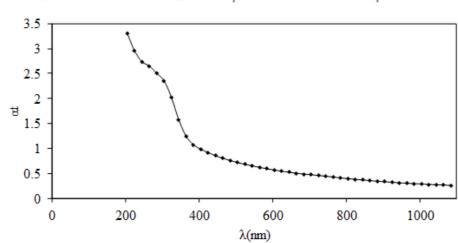
3.1. Optical Analysis: Study of material by means of optical absorption provides a simple method for explaining some features concerning theband structure of material. In the present investigation, optical absorption(Fig.1) in NiO film was studied in the wavelength range 300 to 1100nm. The nature of transition(direct or indirect) is determined by using the relation,

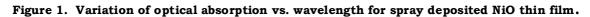
$$\alpha = \frac{A(hv - Eg)^{\mu}}{hv}$$
(1)

Where hu is the photon energy, Eg the band gap energy, A and n are constants. For allowed direct transition, n=1/2 and for forbidden direct transition, n=3/2.

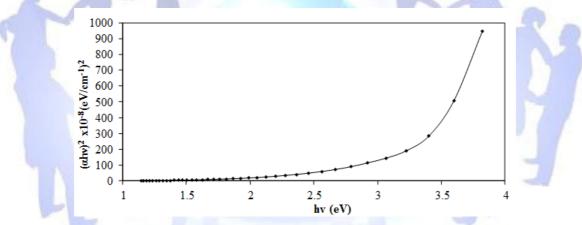


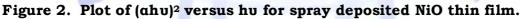
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The plot of $(ahu)^2$ versus hu is shown in Figure 2. Since the variation of $(ahu)^2$ with hu for NiO thin film is a straight line it indicates that the involved transition is direct one. Band gap energy, Eg was determined by extrapolating the straight line portion to the energy axis for zero absorption coefficient (a). The value of Eg for as deposited film was found to be 3.3 eV.





3.2. *Electrical Analysis:* The investigations of electrical transport properties of the deposited material are important in determining the congruency of the material with our necessities. The electrical properties of the nanostructured film depends specially on the film composition and on the various deposition parameters such as substrate temperature, deposition rate, nature of substrate and nature of anionic and cationic precursors used. The two-probe technique of dark electrical conductivity measurement was used to study the variation of electrical conductivity of film with temperature.

The room temperature electrical resistivity is of the order of $10^6 \Omega$ cm. The thermal activation energy was calculated using the relation,

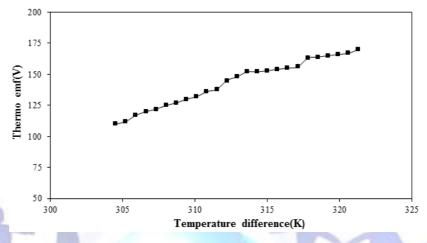
 $\rho = \rho_0 \exp \left(\frac{E_0 / KT}{KT} \right)$ (2)

where, ρ is resistivity at temperature T, ρ_0 is a constant; K is Boltzmann constant. The activation energy (E₀) was calculated from the resistivity plots. The activation energy is found to be 0.110 eV.





3.3. Thermo-emf measurement: Thermo-emf measurement was used to evaluate type of conductivity of dependent material. From the sign of thermo-emf ithas been found that NiO film exhibits n-typeconductivity. Figure 3 shows the variation of thermo-emfwith applied temperature difference. The plot shows thatthermo-emf increase with increasing temperature difference. This may be attributed to the increase inmobility and/or concentration of charge carrier withrise in temperature.



4. Conclusion

In the present paper, optical and electrical properties of nanostructured NiO thin films deposited by chemical spray technique have been reported. Nickel oxide films are nanocrystalline in nature withcubic phase. The optical studies confirmed that spray deposited NiO exhibits 3.3eV band gap energy. The electrical characterization shows that nickel oxide films are semiconducting in nature with ntype conductivity.

References

[1] C. L. Shao, X. H. Yang, H. Y. Guan, Y. C. Liu , J. Gong Inorg. Chem. Comm., Vol. 7, No. 5, 2004, pp. 625-627.

[2] G.J. Li, X.X. Huang, Y. Shi, J.K. Guo, Mater. Lett., Vol. 51, No. 4, 2001, pp. 325-330.

[3] B. Sasi, K. Gopchandran, P. Manoj, P. Koshy, P. Rao ,V. K. Vaidyan, Vacuum, Vol. 68, No. 2, 2003, pp. 149-154.

[4] J. D. Desai, S. K. Min, K. D. Jung, O. S. Joo, J.Appl. Surf. Sci., Vol. 253, No. 4, 2006, pp.1781-1786.

[5] J.K. Kang, S. W. Rhee, Thin Solid Films, Vol. 391, No. 2, 2001, pp. 57-61.

[6] K. Nakaoka, J. Ueyama, K. Ogura, J. Electroanaly. Chemi., Vol. 571, No.1,2004, pp. 93-99.

[7] D. J. Taylor, P. F. Fleig, S. T. Schwab, R. A. Page, J. Surf. Coatings Tech., Vol. 120, 1999, pp. 465-469.

[8] J. L. Garcia-Miquel, Q. Zhang, S. J. Allen, A. Rougier, A. Blyr, H. O. Davies, A. C. Jones, T. J. Leedham, P. A.William, S.A. Impey, Thin Solid Films, Vol. 424, No. 2, 2003, pp.165-170.

[9] J. W. Park, J. W. Park, D. Y. Kim, J. K. Lee, J. Vacuum Sci. Tech. A., Vol. 23, No. 5, 2005, pp.1309-1313.





[10] K. S. Ahn, Y. C. Nah, Y. E. Sung, J. Appl. Surf. Sci., Vol. 199, No. 1-4, 2002, pp. 259-269.

[11] H. L. Chen, Y. M. Lu, W.S. Hwang, Thin Solid Films, Vol. 514, No.1-2,2005, pp. 361-365.

[12] P. Pramanik, S. Bhattacharya, J. Electrochem. Soc., Vol. 137, No. 12, 1990, pp. 3869-3870.

[13] B. Pejova, T. Kocareva, M. Najdoski, I. Grozdanov, J. Appl. Surf. Sci., Vol. 165, No. 4, 2000, pp. 271-278.

[14] A. J. Varkey, A. F. Fort, Thin Solid Films, Vol. 235, No. 1-2, 1993, pp. 47-50.

[15] S. Y. Han, D. H. Lee, Y. J. Chang, S. O. Ryu, T. J. Lee, C. H. Chang, J. Electrochem. Soc., Vol.153, No. 6, 2006, pp. C382-C386.

[16] S. Banerjee, A. Santhanam, A. Dhathathrenyan ,M. Rao, Langmuir, Vol. 19, No. 13, 2003, pp. 5522-5525.





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