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STRUCTURAL, OPTICAL AND ELECTRICAL PROPERTIES OF CHEMICAL BATH DEPOSITED NIO THIN FILMS

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ABSTRACT

NiO thin films have been synthesized by using chemical bath deposition method at various deposition times. The deposited films are further characterized for structural, morphological, optical and electrical properties by XRD, SEM, UV-Visible and two probe techniques respectively. The structural analysis carried out by XRD, shows polycrystalline nature of films with cubic crystal structure. The SEM images shows surface has porous structure with honeycomb like pores. Optical band gap NiO thin film founds to be 3.1 eV. The electrical resistivity of NiO thin films is of the order of 10^5 Ω-cm.

KEYWORDS: NiO thin films, Chemical bath deposition.

INTRODUCTION

In recent years, nanoscience and nanotechnology plays significant role in various applications microelectronics, communications, optoelectronics, integrated optics and photovoltaic devices [1].Thin film science is one most considerable fact of nanotechnology. Many transition metal oxide films were studied for various devices [2]. NiO is one of the transition metal oxides having wide band gap energy in the range 3.6 to4.0 eV. It is a promising candidate with p-type conductivity [3]. The electrical resistivity of undoped stoichiometric NiO thin films is of the order of 10^{13}Ω-cm at room temperature [4]. It is noticed that resistivity can be lowered by doping of monovalent ions. Lithium doped NiO thin film has shown decrease in resistivity up to 10^2Ω-cm [5]. The deposition techniques used to synthesis also affects the resistivity. Jang et al. [6] have prepared the lithium doped NiO thin films by using RF magnetron sputtering by varying lithium concentration in the films resulting into decrease in electrical resistivity. Moghe et al. [7] have reported effect of Cu doping on NiO thin films. The decrease in activation energy and optical band has been observed. NiO has been considered as a promising material with possible applications in different fields, such as solar cells, chemical sensor, electrochromic display devices, smart windows, lasers, luminescent materials, Li ion batteries, and fuel cells [5, 8-9]. Recently NiO thin films are considered as electrode for electrochemical supercapacitor [10-11].

There are several methods for the synthesis of NiO thin films including physical as well as chemical deposition methods. The physical methods used are DC reactive magnetron sputtering [12]and RF sputtering [13] while chemical methods used to deposit NiO thin films are chemical vapor deposition [14], chemical bath deposition [15], sol gel [10], electrodeposition [16],and spray pyrolysis [17]. Among these methods chemical bath deposition technique is a comparatively low-cost, simple thin film synthesis process that is able to produce stiochiometrically accurate crystalline phases. It is a mainly cost effective and convenient technique, which is highly reproducible. The another advantage of this technique is films can be deposited on substrates by dipping them into solution baths containing metal salts without applying any external field [18].

In the present work, we have synthesized NiO thin films using nickel chloride hexahydrate by varying deposition time 45 to 90 min at constant bath temperature of 70ºC. Thermal annealing treatment has been given for 2 hours for all films. Effect of deposition time on structural, morphological, optical and electrical properties has been studied.

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EXPERIMENTAL

The NiO thin films are prepared by a low cost, simple chemical bath deposition technique on thoroughly cleaned glass substrates. The glass substrates provided by blue star of dimension 7.5cm×2.5cm×0.135cm are used. High purity nickel chloride hexahydrate is used as source of Ni. A precursor solution is prepared by using 80 ml of 1M $NiCl_2.6H_2O$, 60ml of 0.1M $K_2S_2O_8$, and 20 ml of aqueous ammonia (25-28%) in 200 ml beaker. The substrates were kept vertically in the deposition bath with constant stirring at 70°C. The deposited films are extracted from deposition bah after 45, 60, 75 and 90 minutes. Then washed with de-ionized water in order to remove loosely bounded particles and further annealed at 300 °C in air for 120 min.

The thicknesses of NiO thin films are determined by well-known weight difference method by using sensitive microbalance. Structural properties are studied by X-ray diffractometer having CuKα radiations with wavelength 1.5406Å. The scanning electron microscopy gives information about surface morphology of NiO thin films. Optical study used to find out band gap of material. The electrical resistivity of the films was studied using a DC two point probe method.

RESULTS AND DISCUSSION

Thickness Measurement

The as-deposited NiO films are annealed at 300 °C in air for 120 min. Film thickness is measured by weight difference method by considering bulk density of NiO material. Variation of film thickness with deposition time is shown in Fig. 1. The maximum thickness of 215 nm is observed for film deposited at 75 minutes. Film thickness increases with increase in deposition time and saturates after 75 min. The irregular variation in growth rate can be attributed to the development of tensile stress that tends to cause delamination when film becomes thick [19].

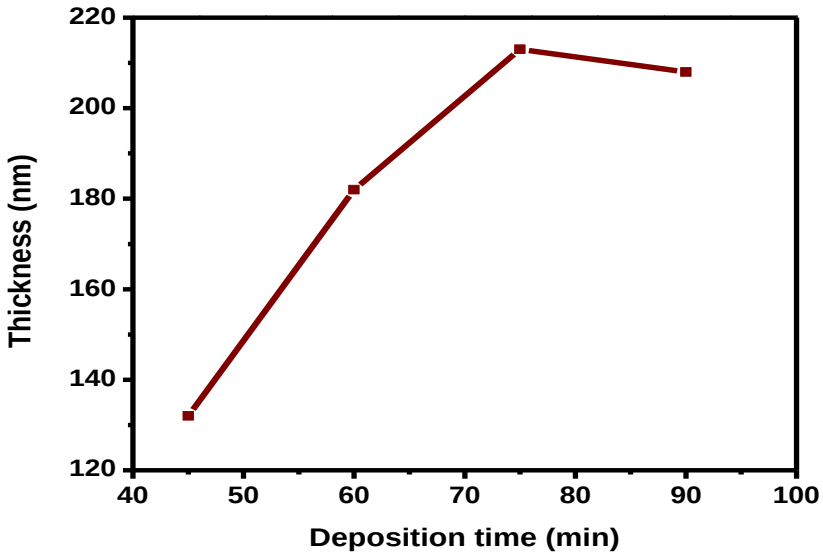

Fig. 1 Variation of film thickness with deposition time of chemically deposited NiO thin films

STRUCTURAL ANALYSIS

In order to study the crystalline phase the chemically deposited NiO thin films XRD pattern are recorded in the 2θ range 10 to 90°. Fig. 2 shows the XRD pattern of NiO thin film deposited for 75 min. The pattern shows polycrystalline nature of film. The peaks observed at 37.5°, 43.5°, 62.9° and 79.4 corresponding to (111), (200), (220) and (222) planes respectively. By matching this peak values with the JCPDS data 47-1049 cubic NiO phase confirmed. The maximum peak intensity is observed at 37.5° showing preferential orientation of NiO film in (111) direction. The observed'd' values are well match with standard 'd' values for all peaks.

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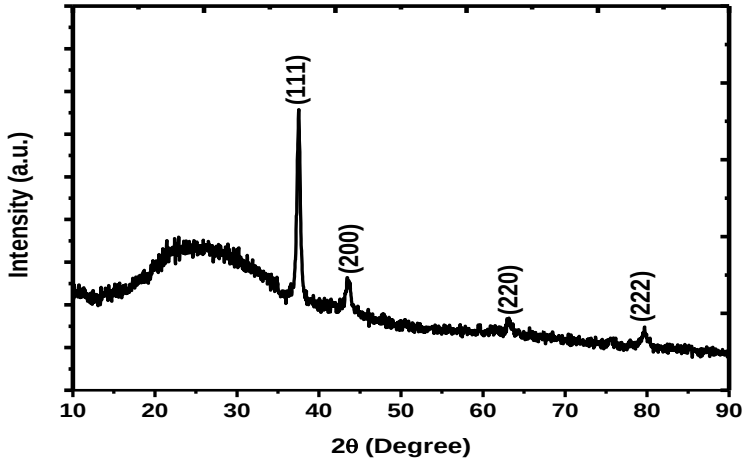

Fig. 2 The XRD pattern of chemically deposited NiO thin film with deposition time 75 min

The lattice constant is calculated for cubic NiO thin films by using relation

$$d^2 = \frac{a^2}{(h^2+k^2+l^2)} \qquad (1)$$

Where d is the interplanner spacing, a is lattice parameter and h,k,l are the miller indices. The average lattice parameter is found to be a=b=c= 4.16Å. The average value of crystalline size (D) for plane (111) is calculated by using Scherer's formula

$$D = \frac{k\lambda}{\beta\cos\theta} \qquad (2)$$

Where k is constant, λ is wavelength of incident radiations, β is full width at half maximum and θ is Bragg's diffraction angle. The estimated crystalline size is about 14 nm. This crystalline size is smaller than 17.68 - 20.24nm reported by Sharma et al. [17].

SURFACE MORPHOLOGY

NiO thin films deposited for 75 min are studied by scanning electron microscopy.Fig.3 shows SEM image of NiO thin film at 2000× magnification. It observed that the surface is covered with inhomogeneous, randomly oriented honeycomb like pores. No cracks are observed on the film surface. The average diameter of pores was observed to be less than 1μm. The image shows there is interconnected flake like structure with large space in between them. The similar flakes of NiO are also observed by Inamdar et al.[15]. Such type of morphology suggest NiO film may be applicable for supercapacitor and gas sensing applications [20]

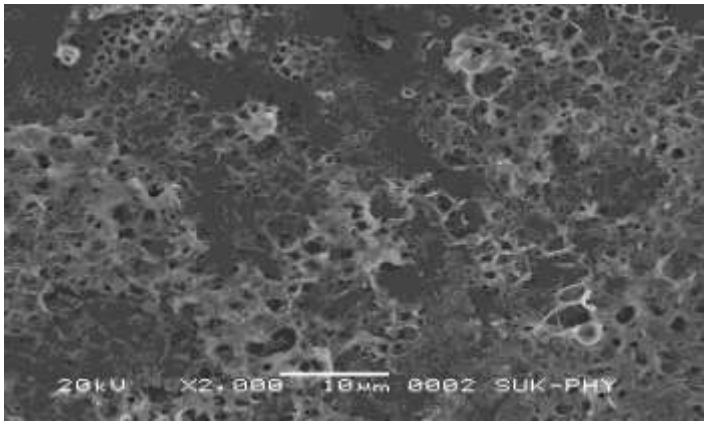

Fig. 3 The SEM images of NiO thin film having magnifications 2000×.

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OPTICAL PROPERTIES

Optical measurements are used to determine the band gap of NiO films. Optical absorption spectrum of NiO thin film in the wavelength range 300–1100nm has been recorded using UV-Visible spectrophotometer. Fig. 4 Plot of $(\alpha h\upsilon)^2$ versus photon energy ($h\upsilon$) for NiO thin films with various deposition times.

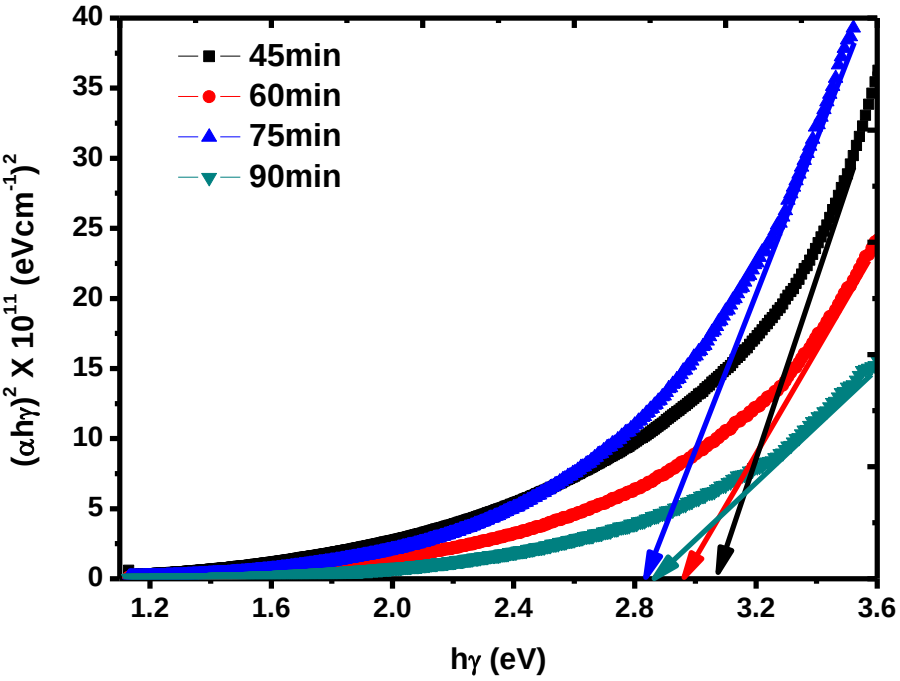

Fig. 4 Plot of (ahy)^2 versus photon energy (hy) for NiO thin films with various deposition times

The band gap energy are obtained from the following relation [21],

$$\alpha h\nu = A(h\nu - Eg)^n \qquad (3)$$

where A is a constant, α is the absorption coefficient, h$\boldsymbol{\nu}$ is the photon energy, Eg is the band gap energy of material and n= ½ for direct allowed transition. The estimated optical band gap decreases from 3.10 to 2.83eV with increase in deposition time. Obtained band gap energies, are in good agreement with the reported values [1].The band gap reported in present study is smaller than 4.0 eV observed for Bulk crystalline NiO. The decrease band gap with increase in film thickness may be due to the change in crystallinity of film [22].The increase in thickness leads to the incorporation of more oxygen atoms in the film. The entry of more oxygen atoms creates extra energy levels in the NiO band gap close to the valence band edge, with a successive reduction of the energy associated with indirect transitions [23].

ELECTRICAL PROPERTIES

DC electrical resistivity of chemically deposited NiO with various film thicknesses are studied with two point probe method. Silver paste is applied for good ohmic contact. The resistivity of films can be measured as a function of inverse of temperature and plotted in Fig.5. It was observed that the resistivity of all films decreases as temperature increases indicating that semiconductor behavior NiO. The resistivity of film decreases as film thickness increases. At lower film thickness more number of defects acts as scattering centre which forms trapping state reduces free carriers available for conduction [24].

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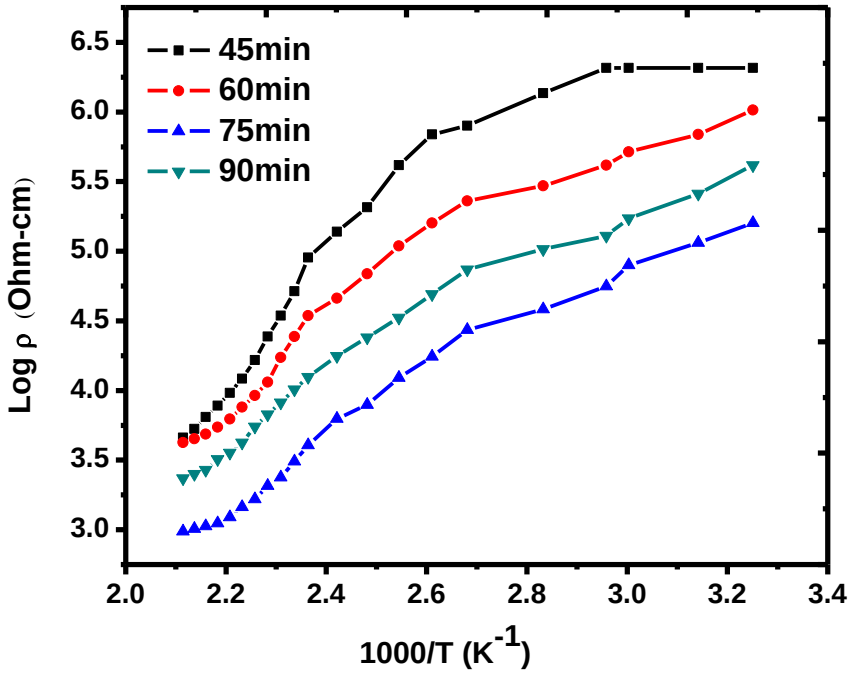

Fig. 5 Electrical resistivity as a function of inverse of temperature of NiO thin film at various deposition times.

The electrical resistivity of NiO thin films at room temperature is observed to be in the range of 10^5 - 10^6 Ω-cm. Activation energy (Ea) was calculated by using the equation

$$\rho = \rho_0 \exp\left(\frac{E_a}{kT}\right) \qquad (4)$$

Where, ρ is the resistivity at temperature T, ρ_0 a constant, k the Boltzmann constant, T the absolute temperature and Ea is the activation energy. The activation energy values at room temperature increases from 0.11eV to 0.23eV as deposition time increases from 45 to 90 min.

CONCLUSIONS

NiO thin films are successfully synthesized by chemical bath deposition method at various deposition times. XRD data gives formation of cubic NiO phase with lattice parameter 4.16Å. Surface morphology has honeycomb like porous structure with pore size less than 1μm. Optical study gives direct bang gap for NiO thin film is 3.1eV. Electrical resistivity decreases with increase in temperature predicts NiO thin film behaves as semiconductor. Average electrical resistivity found of the order of 10^5Ω-cm. These porous NiO thin films may be applicable for supercapacitor.

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REFERENCES

[1] V. Gowthami, P. Perumal, R. Sivakumar, C. Sanjeeviraja. Nickel oxide thin film prepared by nebulizer spray technique. Physics B 452 (2014) 1-6.
[2] A. A. Yadav, Influence of film thickness on structural, optical and electrical properties of spray deposited antimony doped SnO2 thin films, Thin Solid Films 591 (2015) 18-24.

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Impact Factor: 4.116
CODEN: IJESS7

[3] Bin Liu, Heqing Yang, Hua Zhao, LijuanAn, Lihui Zhang, Ruyu Shi, Lin Wang, Liu Bao, Yan Chen, Synthesis and enhanced gas-sensing properties of ultralong NiO nanowiresassembled with NiO nanocrystals, Sensors Actuat. B 156 (2011) 251–262
[4] J.D. Desai, Sun-Ki Min, Kwang-Deog Jung, Oh-Shim Joo. Spray pyrolytic synthesis of large area NiOx thin films from aqueous nickel acetate solutions. Appl. Surf. Sci.253 (2006) 1781–1786.
[5] I.A. Gardunao, J.C .Alonso, M. Bizarro, R. Ortega, L. Rodrıguez-Fernandez, A. Orti. Optical and electrical properties of lithium doped nickel oxide films deposited by spray pyrolysis onto alumina substrates. J. Cryst. Growth 312 (2010) 3276–3281.
[6] Jang Wei-Lung, Lu Yang-Ming, Hwang Weng-Sing, Chen Wei-Chien.Electrical properties of Li-doped NiO films. J..European Ceramic Society 30 (2010) 503-508.
[7] ShwetaMoghe, A.D. Achary, Richa Panda, S.B. Shrivastava, Mohan Gangrade, T. Shripathi, V. Ganesan. Effect of copper doping on the change in the optical absorption behavior in NiO thin films. Renewable Energy 46 (2012) 43-48.
[8] M. Krunks J. Soon, T. Unta, A. Mere, V. Mikl. Deposition of p-type NiO films by chemical spray pyrolysis. Vacuum 107 (2014) 242-246.
[9] R. Romero, F. Martin, J.R. Ramos-Barrado, D. Leinen.Synthesis and characterization of nanostructured nickel oxide thin films prepared with chemical spray pyrolysis. Thin Solid Films 518 (2010) 4499-4502.
[10] Dhanaji S. Dalavi, Rupesh S. Devan, Raghunath S. Patil, Yuan-Ron Ma, Pramod S. Patil. Electrochromic performance of sol–gel deposited NiO thin film. Mater.Lett. 90 (2013) 60-63.
[11] Shuaishuai Zhu, Yuming Dai, Wei Huang, Chuanxiang Zhang, Yuquan Zhao, Linhua Tan, Zhangzhong Wang. In situ preparation of NiO nanoflakes on Ni foams for high performance supercapacitors. Mater.Lett. 161 (2015) 731–734.
[12] Hao-Long Chena, Yang-Ming Lub, Weng-Sing Hwanga Characterization of sputtered NiO thin films. Surf.Coat. Tech. 198 (2005) 138 – 142.
[13] Ivan Hotovy, JozefLiday, Helmut Sitter, Peter Vogrincic. Properties of sputtered NiO thin films. J..Elect. Eng. 53 (2002) 339-342.
[14] PavelMoravec , Jiri Smolík, HelmiKeskinen, Jyrki M. Makela, SnejanaBakardjieva, Valeri V. Levdansky, NiO_xnanoparticle synthesis by chemical vapor deposition from nickel acetylacetonate. Mater. Sci. Appl. 2 (2011) 258-264.
[15] A.I. Inamdar, YoungSam Kim, S.M. Pawar, J.H. Kim, HyunsikIm, Hyungsang Kim. Chemically grown, porous, nickel oxide thin-film for electrochemical supercapacitors.J.Power Sources 196 (2011) 2393–2397.
[16] A.C. Sonavane, A.I. Inamdar, P.S. Shinde, H.P. Deshmukh, R.S. Patil, P.S. Patil. Efficient electrochromic nickel oxide thin films by Electrodeposition, J. Alloys Comp. 489 (2010) 667–673.
[17] Ratnesh Sharma, A.D. Acharya, S.B. Shrivastava, T. Shripathi, V. Ganesan, Preparation and characterization of transparent NiO thin films deposited by spray pyrolysis technique, Optik 125 (2014) 6751–6756.
[18] S.U. Offiah, A.C. Nwanya, S.C. Ezugwu, B.T. Sone, R.U. Osuji, Maaza Malik, C.D. Lokhande, F.I. Ezema, Chemical bath synthesis and physico-chemical characterizations of NiO-CoO composite thin films for supercapacitor applications, Int. J. Electrochem. Sci., 9 (2014) 5837 – 5848.
[19] S.G. Kandalkar, D.S. Dhawale, Chang-Koo Kim, C.D. Lokhande, Chemical synthesis of cobalt oxide thin film electrode for supercapacitor application, Synthetic Metals 160 (2010) 1299–1302
[20] A. A. Yadav, Influence of electrode mass-loading on the properties of spray deposited Mn_3O_4 thin films for electrochemical supercapacitors, Thin Solid Films 608 (2016) 88–96
[21] A.A. Yadav, T.B. Deshmukh, R.V deshmukh, D.D. Patil, U.J.Chavan, Electrochemical supercapacitive performance of Hematite α-Fe_2O_3 thin films prepared by spray pyrolysis from non-aqueous medium, Thin solid films 616 (2016) 351-358.
[22] A.A. Yadav, Preparation and electrochemical properties of spray deposited α-Fe2O3 from non aqueous medium for supercapacitor applications, J Mater Sci: Mater Electron (2016). doi:10.1007/s10854-016-5423-3.
[23] M. Jlassi, I.Sta, M.Hajji, H.Ezzaouia,Optical and electrical properties of nickel oxide thin films synthesized by sol–gel spin coating, M. Sci. Semicond. Process. 21 (2014) 7–13
[24] Y. Akaltun, T. Çayir. Fabrication and characterization of NiO thin films prepared by SILAR method, J. Alloys Compd. 625 (2015) 144-148.