Structural, Optical and Electrical Properties of NiO Thin Films Prepared by Low Cost Spray Pyrolysis Technique

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***Abstract*—Nickel Oxide (NiO) thin films are fabricated using fresh and aged precursor solutions using a low cost simplified spray pyrolysis technique. Structural, optical and electrical properties of two different films were studied. The structural studies show that the film prepared from the aged solution has more grain size (60.3nm) than the film prepared by fresh solution (21nm). From the optical studies it is found that, the band gap of film from fresh solution have 3.6eV while the band gap of film from aged solution is about 3.5eV. The refractive index (n) is measured with the help of PUMA software and for the film from fresh solution it remains at 1.95 through visible region. However, for the film from aged solution, it varies from 2 to 1.78 in visible region. The calculated extinction coefficient (k) values of the films show no significant variation in visible and NIR range. The electrical studies confirm that the grown films are p-type. The resistivity measured for two films shows that the resistivity is low ($2.271\times10^2\Omega$ cm) for the film prepared by fresh solution and it is high ($2.725\times10^2\Omega$ cm) for the other one.**

***Index Terms*—NiO thin films, perfume atomizer, optical studies, refractive index, electrical studies**

I. Introduction

Nickel oxide (NiO) is a promising p type semiconducting oxide material [1], [2] having a wide band gap of 3.6eV to 4eV [3]. It resembles NaCl structure with octahedral Ni (II) and (O2-) sites [4]. Due to its enormous potential applications such as, anti-ferromagnetic material [5], [6], chemical sensors [7], electrochromic devices [8], catalysts [9], dye sensitized solar cells (DSSCs) [10], it attracts the researchers attention towards it. NiO thin films were fabricated using many methods such as electron beam evaporation [11], reactive sputtering [12], plasma enhanced chemical vapour deposition [13], pulsed laser deposition [14], spray pyrolysis [15], chemical bath deposition [16] etc. Among various methods, spray pyrolysis is one through which the films can be coated for large area. In this present work a low cost and simplified spray pyrolysis technique using perfume atomizer [17]-[19] is employed to fabricate the NiO thin films. The aging effects of the precursor solution on the optical and electrical properties of the grown films are studied and discussed.

II. Experimental Detail

A set of precursor solution is prepared using Nickel acetate tetrahydrate ($Ni\ (C_2H_3O_2)_2.4H_2O$) with 0.1 molarity in ethanol mixed deionized water. One of them is allowed to age about 24 hours and the other one (fresh solution) is taken into use to form NiO film (Sample 1). The second solution (aged solution) is taken after 24 hours and then the second NiO film is fabricated (Sample 2). The volume for both solutions is about 50ml. The substrates used were glasses. The substrates are cleaned in distilled water and then dried using air blower. After that they were cleaned again with acetone in order to remove any strains on it. The solutions were then sprayed manically on the glass substrates with air as carrier gas. The temperature was set to 330 ℃. The temperature chosen is due to the acetate in the precursor will decompose above 300 ℃. Due to continuous spraying, the substrate temperature is suddenly reduced to 310 ℃ to 320 ℃. Therefore, after every 5 spray, the process was stopped about 5 minutes to recover the substrate temperature to 330 ℃.

X-ray diffraction analyses were obtained using the model X‟pert PRO (PANalytical) X-ray powder diffractometer with Ni filtered CuKα (1.5406Å) radiation for a range of 10º to 90º 2θ angles. The surface morphology, homogeneity and grain size of the deposited films were studied by SEM model JSM 35 CF JEOL. The optical studies were carried out by Perkin Elmer Lambda 35 UV-VIS-NIR double beam spectrophotometer for a wavelength range of 300nm to 1100nm. Hall effect measurement was carried out with Ecopia HMS 5000 Hall effect measurement system. Thicknesses of the films were measured gravimetrically and the measured thicknesses are 631nm and 676nm for Sample 1 and Sample 2 respectively.

III. Results and Discussion

Manuscript received September 9, 2013; revised December 30, 2013.

doi: 10.12720/ijmse.1.2.118-121

A. *Structural Characteristics*

The x-ray diffractograms of the fabricated NiO films are shown in Fig. 1. The peaks are observed at 35.94, 42.67 and 62.18 2θ values for the first film (Sample 1), and for the second film (Sample 2) 36.362, 43.43, and 62.58 2θ values are observed and they are corresponds to (111), (200) and (220) crystal planes respectively which belong to NiO cubic structure (JCPDS card no. 89-7130).

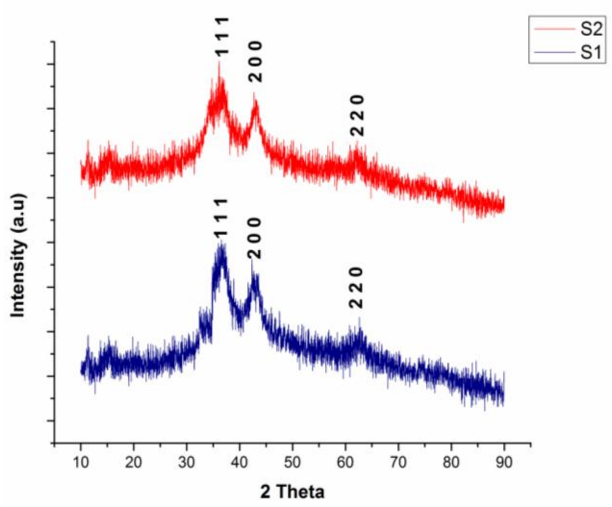

Figure 1. X-Ray difractogram of NiO thin films

The average particle size is calculated using Scherrer formula [20]

$$D=0.91\lambda/\beta \cos \theta \qquad (1)$$

where λ wavelength of x-ray, β is the FWHM (full width at half maximum intensity) and θ is Bragg's angle. The calculated average particle size for Sample 1 is about 21nm and for Sample 2 is 60.3nm.

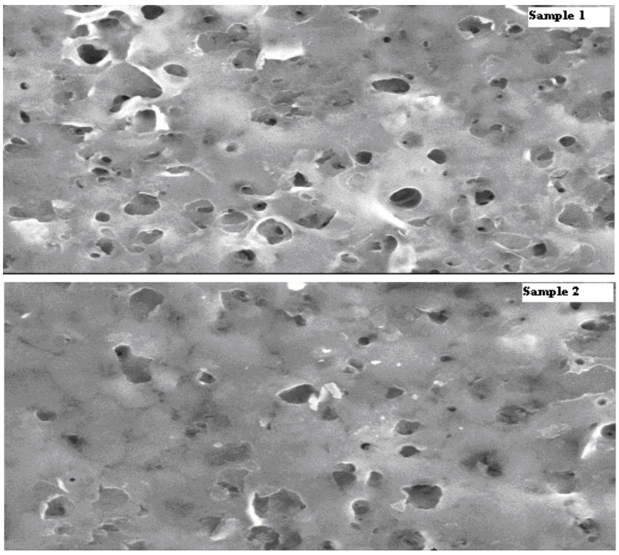

Figure 2. SEM images of NiO thin films

The microstructures of the prepared NiO thin films are shown in Fig. 2. The SEM images show that the films are formed well with sticky nature with substrate. There are no cracks observed on the film surfaces. It is noted that for the film formed without aging of precursor solution (Sample 1) exhibit clear and smooth grains. However, the film formed with aging solution (Sample 2) shows greater grain size.

B. *Optical Properties*

Fig. 3 shows the transmission spectra of Sample 1 and Sample 2. For both samples the absorption edge is found around 350nm. The observed transmission for Sample 1 is greater than the Sample 2 which results that the aged solution has lesser transparency.

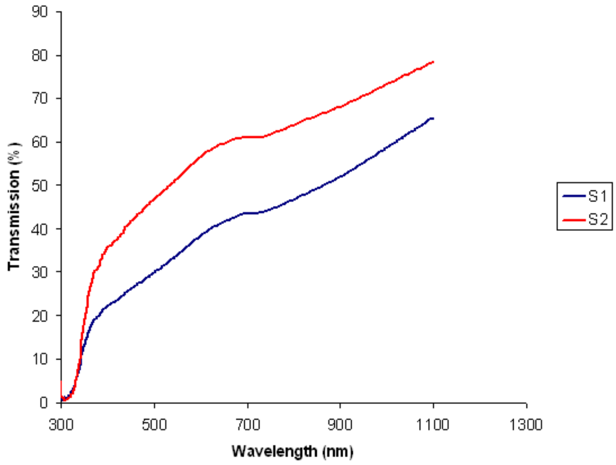

Figure 3. Transmission spectra of NiO thin films

The optical band gap of the NiO film samples can be calculated by plotting (αhν) 2 versus photon energy (hν) is shown in Fig. 4. The calculated band gap for Sample 1 is 3.6eV where as for the Sample 2 (from aged solution) it is decreased and it is found to be 3.5eV. From the results, it is observed that, for Sample 2 the grain size is increased due to aging effect of precursor solution and hence results the decreasing band gap.

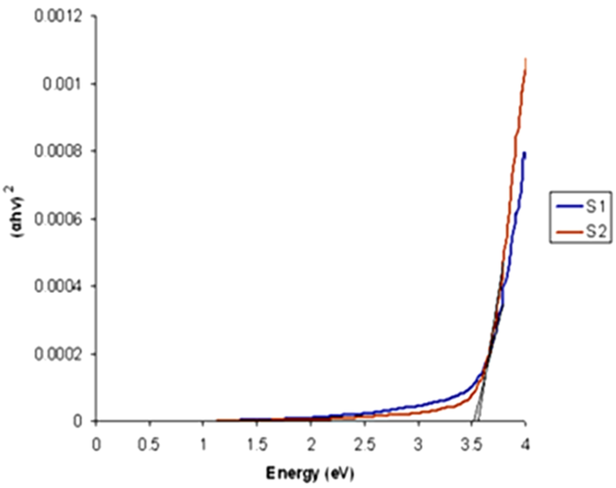

Figure 4. Optical band gap spectra of NiO thin films

The refractive index (n) of the prepared NiO films have been calculated using PUMA [21], a freeware software based on pointwise unconstrained minimization approach, for a range of wavelength of 300nm to 1100nm. The plot of wavelength versus n is shown in Fig. 5. For the Sample 1, the refractive index of the film remains almost equal through the visible region with the value of 1.95 which is slightly lesser value from the earlier reported values [22]. For the sample 2, the refractive index value drastically decreases upto 400nm and then it remains constant at 1.77.

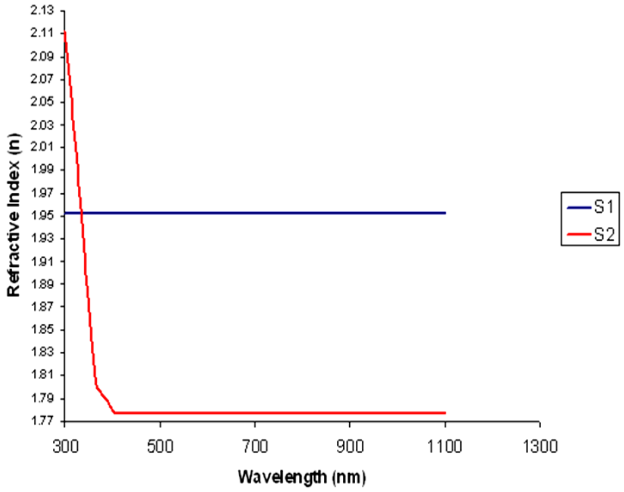

Figure 5. Variation of refractive index (n) with wavelength of NiO thin films

From the calculated absorption coefficient (α) values the extinction coefficient of the films were calculated over visible and NIR wavelengths using the following formula:

$$k=\alpha\lambda/4\pi \text{ [23]} \qquad (2)$$

where λ is the wavelength. A plot between wavelength and absorption coefficient is shown in Fig. 6. From the figure it is clear that the extinction coefficient varies in the uv region. However, it is almost constant in the visible and NIR range for both films.

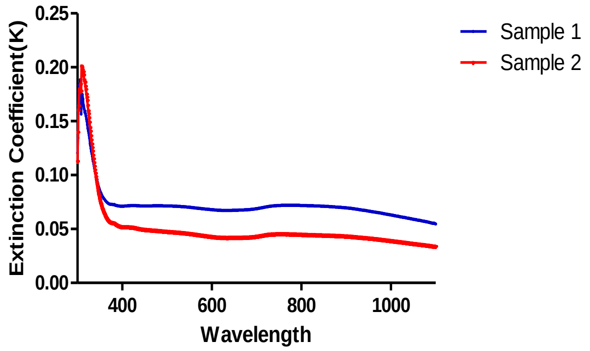

Figure 6. Extinction coefficient vs wavelength of NiO thin films

From the calculated values of extinction coefficient, it is clear that the grown films are not strong absorbing medium in the UV and NIR wavelength region.

C. Theoretical Validation of Refractive Index

The refractive index of the deposited samples of NiO thin films calculated by PUMA has been validated using the relation between energy gap and refractive index formula:

$$n=\sqrt{12.417/(E_g-0.365)} \text{ [24]} \qquad (3)$$

where E_g is the energy gap of the film. Using the above relation, the refractive index calculated for sample 1 is 1.95 and for sample 2 is 1.99 from the calculated energy gaps of the film samples. They are in good agreement with the calculated value by PUMA.

D. Electrical Properties

From the Hall effect measurement it is confirmed that the grown films are p-type. The Table I shows the measured values of Hall coefficient, resistivity, conductivity and mobility of the film samples.

TABLE I. ELECTRICAL PROPERTIES OF NIO THIN FILMS

Sample	Thickness (nm)	μ (cm^2/Vs)	σ (1/Ω cm)	ρ (Ω cm)	R_H (cm^3/C)	Type
Sample 1	631	14.73	4.409×10^{-3}	2.271×10^{2}	3.342×10^{3}	P
Sample 2	676	11.715	3.669×10^{-3}	2.725×10^{2}	3.193×10^{3}	P

μ-mobility, σ-conductivity, ρ-resistivity & R_H-Hall coefficient.

For Sample 1, the measured resistivity is about 2.271×10^2Ω cm and for Sample 2 it is about 2.725×10^2Ω cm. The measured Hall coefficient values for Sample 1 and Sample 2 are 3.342×10^3 and 3.193×10^3 respectively. From the observed resistivity of Sample 1 and Sample 2 aging effect of precursor solution increases the resistivity and results in decrease in conductivity. The calculated mobility for Sample 1 is 14.73cm^2/Vs and 11.715cm^2/Vs for Sample 2.

IV. CONCLUSION

P type Nickel oxide thin films were fabricated using nickel acetate as precursor solution. The physical properties such as structural, optical and electrical are varying depend upon the aging of precursor solution. If the precursor is allowed to age, the grain size may decrease and hence in decrease in the band gap. The refractive index values are calculated for a range of 300nm to 1100nm. For the film prepared without aging precursor, the refractive index is found to be 1.95 while for the film prepared with aged precursor it varies from 2 to 1.78. The values of extinction coefficient (k) of the films show not much variation in the Visible and NIR range. The electrical studies for the prepared films confirm the p-type conductivity and the resistivity increases when the precursor solution is allowed to age.

REFERENCES

[1] M. Guziewicz, *et al.*, "Electrical and optical properties of NiO films deposited by magnetron sputtering," *Optica Applicata*, vol. XLI, no. 2, pp. 431-440, 2011.

[2] M. K. Lee and Y. T. Lai, "Characterization of transparent conducting p-type nickel oxide films grown by liquid phase deposition on glass," *J. Phys. D: Appl. Phys*., vol. 46, no. 5, 2013.

[3] P. S. Patil and L. D. Kadam, "Preparation and characterization of spray pyrolyzed nickel oxide (NiO) thin films," *Appl. Surf. Sci.*, vol. 199, pp. 211-221, 2002.

[4] N. S. Das, B. Saha, R. Thapa, G. C. Das, and K. K. Chattopadhyay, "Band gap widening of nanocrystalline nickel

oxide thin films via phosphorus doping," *Physica E*, vol. 42, no. 5, pp. 1377-1382, 2010.

[5] P. Mallick and N. C. Mishra, "Evolution of structure, microstructure, electrical and magnetic properties of nickel oxide (NiO) with transition metal ion doping," *American Journal of Materials Science*, vol. 2, no. 3, pp. 66-71, 2012.

[6] L. Albertst and E. W. Lee, "Magnetostriction in antiferromagnetic nickel oxide," *Proc. Phys. Soc.*, vol. 78, pp. 728-733, 1961.

[7] M. Stamataki, D. Tsamakis, N. Brilis, I. Fasaki, A. Giannoudakos, and M. Kompitsas, "Hydrogen gas sensors based on PLD grown NiO thin film structures," *Phys. Stat. Sol. (A)*, vol. 205, no. 8, pp. 2064-2068, 2008.

[8] H. Kamal, E. K. Elmaghraby, S. A. Ali, and K. Abdel-Hady, "The electrochromic behavior of nickel oxide films sprayed at different preparative conditions," *Thin Solid Films*, vol. 483, pp. 330-339, 2005.

[9] W. Azelee, W. Abu Bakar, M. Yusuf Othman, R. Ali , C. Yong, and S. Toemen, "The investigation of active sites on nickel oxide based catalysts towards the in-situ reactions of methanation and desulfurization," *Modern Applied Science*, vol. 3, no. 2, pp. 35-43 ,2009.

[10] J. Bandara and H. Weerasinghe, "Solid-state dye-sensitized solar cell with p-type NiO as a hole collector," *Sol. Energy Mater. Sol. Cells*, vol. 85, no. 3, pp. 385-390, 2005.

[11] D. Y. Jiang, J. M. Qin, X. Wang, S. Gao, Q. C. Liang, and J. X. Zhao, "Optical properties of NiO thin films fabricated by electron beam evaporation," *Vacuum*, vol. 86, no. 8, pp. 1083-1086, 2012.

[12] I. Hotovq, D. Buc, S. Hascik, and O. Nennewitz, "Characterization of NiO thin films prepared by reactive sputtering," *Vaccum*, vol. 50, pp. 41-44, 1998.

[13] E. Fujii, A. Tomozawa, H. Torii, and R. Takayama, "Preferred orientations of NiO films prepared by plasma-enhanced metalorganic chemical vapor deposition," *Jpn. J. Appl. Phys*., vol. 35, pp. L328-L330, 1996.

[14] I. Fasaki, A. Koutoulaki, M. Kompitsas, and C. Charitidis, "Structural, electrical and mechanical properties of NiO thin films grown by pulsed laser deposition," *Appl. Surf. Sci.*, vol. 257, no. 2, pp. 429-433, 2010.

[15] L. Cattin, B. A. Reguig, A. Khelil, M. Morsli, K. Benchouk, and J. C. Bernede, "Properties of NiO thin films deposited by chemical spray pyrolysis using different precursor solutions," *Appl. Surf. Sci.*, vol. 254, no. 18, pp. 5814-5821, 2008.

[16] X. H. Xia, J. P. Tu, J. Zhang, X. L. Wang, W. K. Zhang, and H. Huang, "Electrochromic properties of porous NiO thin films prepared by a chemical bath deposition," *Sol. Energy Mater. Sol. Cells*, vol. 92, no. 6, pp. 628-633, 2008.

[17] K. Ravichandran and P. Philominathan, "Fabrication of antimony doped tin oxide (ATO) films by an inexpensive, simplified spray technique using perfume atomizer," *Mater. Lett*., vol. 62, pp. 2980-2983, 2008.

[18] S. Sriram and A. Thayumanavan, "Optical and electrical properties of nitrogen doped ZnO thin films prepared by low cost spray pyrolysis technique," *Journal of Electron Devices*, vol. 15, pp. 1215-1224, 2012.

[19] B. A. Reguig, A. Khelil, L. Cattin, M. Morsli, and J. C. Bernede, "Properties of NiO thin films deposited by intermittent spray pyrolysis process," *Appl. Surf. Sci*., vol. 253, no. 9, pp. 4330-4334, 2007.

[20] M. Abdullah and Khairurrijal, "Derivation of scherrer relation using an approach in basic physics course," *Jurnal Nanosains & Nanoteknologi*, vol. 1, no. 1, pp. 28-32, 2008.

[21] E. G. Birgin, I. Chambouleyron, and J. M. Mart ńez, "Estimation of optical constants of thin films using unconstrained optimization," *Journal of Computational Physics*, vol. 151, no. 2, pp. 862-880, 1999.

[22] F. Saadati, A.-R. Grayeli, and H. Savaloni, "Dependence of the optical properties of NiO thin films on film thickness and nano-structure," *Journal of Theoretical and Applied Physics*, vol. 4, no. 1, pp. 22-26, 2010.

[23] Han-Yong Joo, Hyeong Joon Kim, Sang June Kim, and Sang Youl Kim, "Spectrophotometric analysis of aluminum nitride thin films," *J. Vac. Sci. Technol. A*, vol. 17, no. 3, pp. 862-870, 1999.

[24] R. R. Reddy, Y. Nazeer Aharnmed, P. Abdul Azeem, K. Rama Gopal, B. Sasikala Devi, and T. V. R. Rao, "Dependence of physical parameters of compound semiconductors on refractive index," *Defence Science Journal*, vol. 53, no. 3, pp. 239-248, July 2003.

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