NANOCRYSTALLINE NiO THIN FILMS PREPARED BY A LOW COST SIMPLIFIED SPRAY TECHNIQUE USING PERFUME ATOMIZER

A.R. Balu [a], V.S. Nagarethinam [a], N. Arunkumar [b], M. Suganya [a],
[a] Department of Physics, A.V.V.M Sri Pushpam College, Poondi, India
[b] Department of Physics, Parisutham Institute of Technology, Thanjavur, India
rajavelubalu@yahoo.com

ABSTRACT

Nickel oxide thin films have been prepared with different molarities of nickel chloride onto ultrasonically cleaned glass substrates kept at 350ºC by a simplified, economical spray technique using perfume atomizer. In this technique atomization is based on hydraulic pressure instead of compressor air pressure as in the conventional spray technique. The X-ray diffraction study reveals that the films are polycrystalline in nature with cubic structure. Micro structural parameters were calculated from the XRD data. Analysis of the absorption versus photon energy curves revealed an indirect transition and the band gap decreases with the increase in solution concentration. Electrical resistivity measurements showed that the magnitude of temperature coefficient of resistance for the films coated with 0.2 M was very low (-1.34×10^{-3} / K). All the above mentioned properties obtained by this simplified technique were found to be fairly comparable with that of their conventional spray counterparts.

Keywords: Perfume atomizer; thin films; NiO; XRD; SEM; Optical absorption.

I. INTRODUCTION

The interest in nickel oxide (NiO) thin films is growing fast due to their importance in many applications in science and technology. Nickel oxide is an anodic electro chromic material (EC), which colors upon reduction (ion extraction). It exhibits large dynamic range and high electro chromic efficiency [1]. The phenomenon of anodic coloration of nickel oxide allows potential applications of this material as a counter electrode in conjunction with tungsten oxide as working electrode in assembling EC device. This has the advantage of increasing the optical density variation of the device, since both electrode colors and bleach simultaneously. Besides acting an EC material, it can also be used as a functional layer material for gas sensors [2]. Other important applications of nickel oxide include preparation of alkaline batteries (as a cathode material), antiferromagnetic layers and p-type transparent conducting films [3-6]. Due to the wide band gap (3.6 – 4.0 eV), it has a wide range of applications in optoelectronics as well as in thermal applications.

Nickel oxide films are a new optical recording material of Ni-NiO heterogeneous systems that would realize portable medium by using a laser diode beam for recording and reading. The new medium needs no protection because of its stability against atmosphere corrosion agents, unlike conventional materials like tellurium [7]. Stoichiometric NiO is an insulator with a resistivity of the order of 10^{13} ohm cm at room temperature [8]. Various methods have been used to prepare nickel oxide thin films including thermal evaporation [9], RF magnetron sputtering [10], electrochemically deposited films [11], chemical vapor deposition [12], pulsed layer deposition [13], electron-beam evaporation [14], atomic layer epitaxy [15], sol-gel [16], spray pyrolysis [17] and anodic deposition [18]. Quite

recently [3], thin films of nickel oxide have been deposited onto glass substrates from chemical route containing Ni^{2+} ion and urea.

In the present work, poly-crystalline films of NiO have been deposited onto glass substrates kept at 350ºC by employing an inexpensive simplified spray technique using a perfume atomizer. In conventional spray technique, usually carrier gas or air is used for spraying the precursor solution. But in this simplified spray technique using perfume atomizer there is no need for the compressed air or any carrier gas and atomization takes place due to hydraulic pressure created inside the spray bottle. The other advantages of this technique are: very low cost, fine atomization avoiding large droplets, uniform coating over large area is possible and enhanced wettability between sprayed micro particles and the previously deposited layers. Sawada et al. [19] and Fukano et al. [20] have established that this simplified spray technique can be successfully used for producing low cost TCO films at relatively low substrate temperatures compared with the conventional spray method. Influence of solution concentration on the micro structural, morphological, optical and electrical properties of the coated NiO films have been investigated and the results are discussed.

II. EXPERIMENTAL DETAILS

NiO thin films were prepared by spraying aqueous solution of high purity nickel chloride [Qualigens make] as precursor salt with different molarities (0.1 M, 0.2 M and 0.3 M) onto ultrasonically cleaned glass substrates. For each deposition 100 ml of solution was sprayed using perfume atomizer onto substrates kept at 350ºC. Micro glass slides were used as substrates in the present work. Substrate cleaning plays an important role in the deposition of thin films. The glass slides were boiled in chromic acid for 30 minutes, degreased with HNO_3 solution, washed with detergent, rinsed in acetone and dried in open air before use. This process is to ensure a clean surface, which is necessary for formation of nucleation centers, required for film deposition. In this simplified spray technique, the atomization is based on hydraulic pressure. The intermittent spray deposition followed in this study is a two step procedure: a spray for 5 sec and an interval for 10 sec. The interval may be increased or decreased to keep the substrate temperature constant, as the deposition temperature is an important parameter which influences the properties of the coated film. The optimum deposition parameters applied for the preparation of nickel oxide thin films are presented in Table 1.

Table 1: Deposition parameters applied in this work.

| Substrate temperature	350ºC
Substrate to nozzle distance	28 cm
Spray angle with respect to the plane of the substrate	45º
Spray rate	0.16 ml/spray
Spray time during each cycle	5 sec
Time interval between successive sprays	10 sec

The thickness of the as-deposited samples was measured using the surftest SJ – 301 stylus type surface roughness and thickness measuring instrument.
X-ray diffraction analyses were obtained using the model X'pert PRO (PANalytical) X-ray powder diffractometer with Ni filtered CuK_{α} (1.5406 Å) radiation. The surface morphology, homogeneity and grain size of the deposited films were studied by SEM model JSM 35 CF JEOL. Optical absorption measurements were carried out by using a Hitachi – 3400 UV-Vis-NIR Spectrophotometer. The electrical resistivity (ρ) of the films was measured by the Vander Pauw four point probe method.

III. RESULTS AND DISCUSSION

III.1 Film formation

The precursor solution was atomized to form uniform stream of fine droplets using perfume atomizer. The pyrolytic decomposition of the fine droplets of aqueous solution of nickel chloride on the glass substrates results in the formation of clusters of NiO. The possible chemical reaction is as follows:

$$NiCl_2 + H_2O \longrightarrow NiO \downarrow + 2\ HCl$$
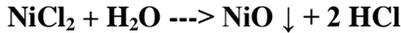
The film thickness was found to be equal to 0.213 μm, 1.012 μm and 2.33 μm for the films coated with 0.1 M, 0.2 M and 0.3 M respectively. It was observed that as the solution concentration increases, the film thickness increases as the amount of material that participates in forming the deposited film increases.

III.2 Structural properties

X-ray diffraction (XRD) patterns of the NiO films coated with 0.2 M and 0.3 M at 350ºC were recorded by varying diffraction angle (2θ) from 30º to 80º, with the step width of 0.02º, whereas for the films coated with 0.1 M it was recorded between 20º to 80º. Fig 1(a, b) shows the XRD patterns of the as-deposited samples with different solution concentrations.
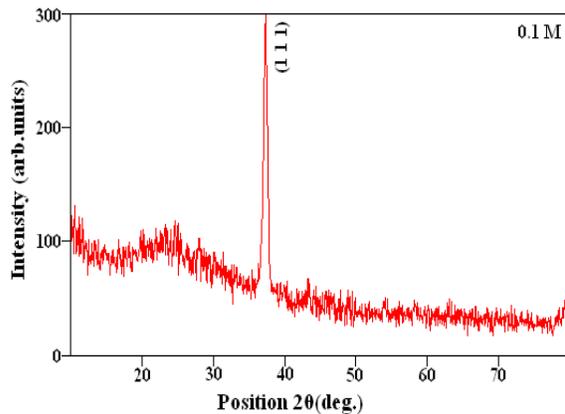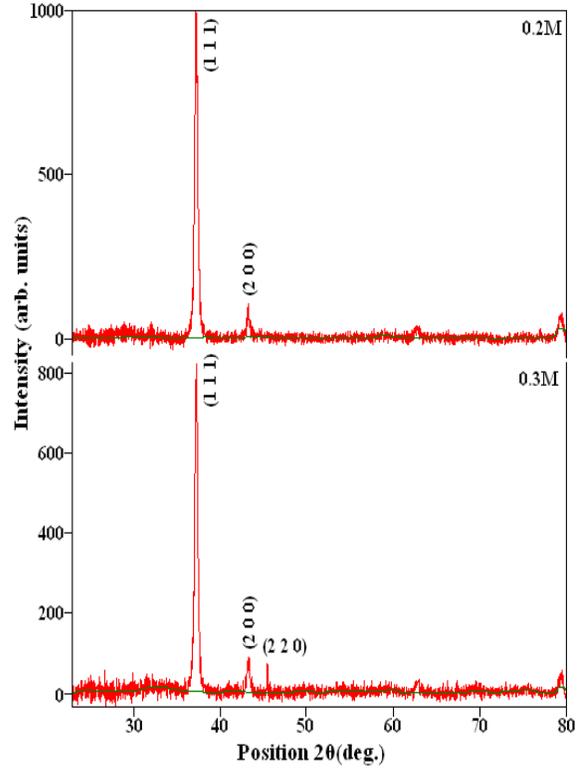
Fig 1(a)

Fig 1(b)

Figure 1(a,b): XRD patterns of NiO thin films coated with 0.1 M, 0.2 M and 0.3 M of solution concentration.

The films coated with 0.2 M and 0.3 M of solution concentration showed well defined peaks having orientations in the (1 1 1) and (2 0 0) planes with growth along the (1 1 1) plane being dominant. This reveals that the films are polycrystalline in nature which belongs to cubic NiO phase [21]. However, films coated with 0.1 M appears to be slightly amorphous with an intense peak at 2θ = 37.27º with preferred orientation being (1 1 1). Other peaks are also observed but they all are within the noise level. The X-ray diffraction data further showed that peak intensity of the plane (1 1 1) was maximum for the films deposited with 0.2 M, indicating the better crystallinity of the films coated with that molarity.

The preferential orientation factor for the (1 1 1) plane relative to other observed peaks are calculated by evaluating the fraction of the intensity of that particular plane over the sum of the intensities of all the other peaks within the 2θ range 20 - 80º. The

922

variation in preferential orientation factor f(h k l) for

(1 1 1) plane as a function of solution concentration in the starting solution is shown in Fig 2, which shows that the

f(1 1 1) increases linearly up to 0.2 M concentration and then it slightly decreases for higher solution concentration which shows the better crystallinity of the films coated with that molarity.
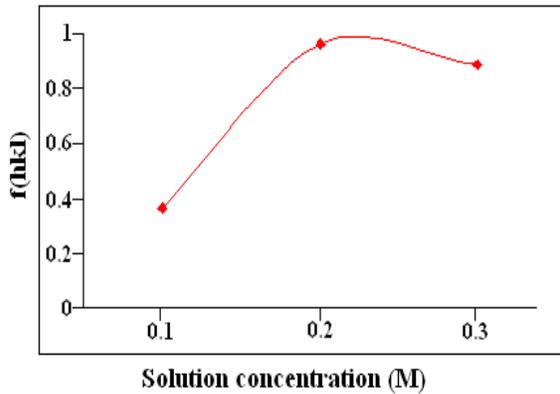

Figure 2: Variation in preferential orientation factor of (111) plane as a function of solution concentration.

The diffraction peaks arising from NiO films coated with 0.2 M solution concentration appear at $2\theta = 37.19°$ and $43.19°$, which are values reported for cubic NiO [**22, 23**]. The observed'd' values are in good agreement with standard'd' values taken from ICDD Card No [**24**]. The results obtained in this work are shown in Table 2 which are in good agreement with those reported earlier by others [**25, 26**], and the above results were attained at a very low temperature compared to the conventional spray counterparts which is the major advantage of this technique.

Table 2: Interplanar distance (d) values of NiO films.

hkl	d standard Å	D (obs) Å		
		Solution concentration		
		0.1 M	0.2 M	0.3 M
(1 1 1)	2.410	2.411	2.415	2.410
	$2\theta = 37.2°$	$2\theta = 37.3°$	$2\theta = 37.2°$	$2\theta = 37.3°$
(2 0 0)	2.09	----	2.093	2.091
	$2\theta = 43.2°$		$2\theta = 43.2°$	$2\theta = 43.2°$
(2 2 0)	1.475	----	1.478	1.476
	$2\theta = 45.3°$			$2\theta = 45.5°$

The lattice parameter 'a' evaluated for the films coated with different solution concentration is shown in Table 3.

Table 3: Lattice constants of NiO films coated at 350ºC with different solution concentrations.

Solution concentration (M)	Lattice constants (Å)	
	Calculated	Standard
0.1	4.176	4.181
0.2	4.183	
0.3	4.174	

There is a strong dependence of the lattice parameter values on the solution concentration. The lattice constant for the film coated with 0.2 M matches with the standard value [**21**] indicating the better crystallinity of the films coated with that molarity. The lattice parameters evaluated from various crystallographic planes have the following systematic observations:

$(a_{111})_{0.1M} < (a_{111})_{0.2 M} > (a_{111})_{0.3 M}$,

$(a_{200})_{0.2 M} < (a_{200})_{0.3 M}$,

$(a_{200})_{0.2 M} < (a_{200})_{0.3 M}$.

Various microstructural properties such as strain in the sample 'ε_s', crystallite size 'D', dislocation density 'δ' and the

number of crystallites 'N' have been calculated using the relations (1-4):

$$\varepsilon_s = \frac{\beta Cos\theta}{4} \qquad (1)$$

$$D = \frac{0.94\lambda}{\beta Cos\theta} \qquad (2)$$

$$\delta = \frac{1}{D^2} \qquad (3)$$

$$N = \frac{t}{D^3} / \text{unit area} \qquad (4)$$

The above parameters were determined using full-width half-maximum (FWHM) of slow scan of the XRD peaks (1 1 1) and the results are compiled in Table 4.

Table 4. Microstructural parameters of NiO films coated at 350ºC with different molarities of solution concentrations.

Micro-structural parameters	Solution concentration		
	0.1 M	0.2 M	0.3 M
Strain, ε_s (x 10^{-3})	2.506	1.1805	2.384
Crystallite size, D (nm)	14.23	30.22	42.31
Dislocation density, δ (x 10^{15} lines/m^2)	1.938	1.095	0.5586
Number of crystallites, N (x 10^{17} /unit area)	0.0692	0.2004	0.087

It has been observed that with an increase in solution concentration, the diffraction lines become more and more sharp, thus apparently showing an increase in the size of the crystallites. Further it is observed, that with the increase in crystallite size, dislocation density decreases. This decrease in dislocation density increases the mobility of the films with higher solution concentration. Films coated with 0.2 M has the least value of strain which increases the

amount of atoms being fixed in the lattice, as the number of crystallites occupying per unit area increases for the films coated with that molarity. This might be the improvement of crystallinity of the films coated with that molarity.

III.3 Surface morphological studies

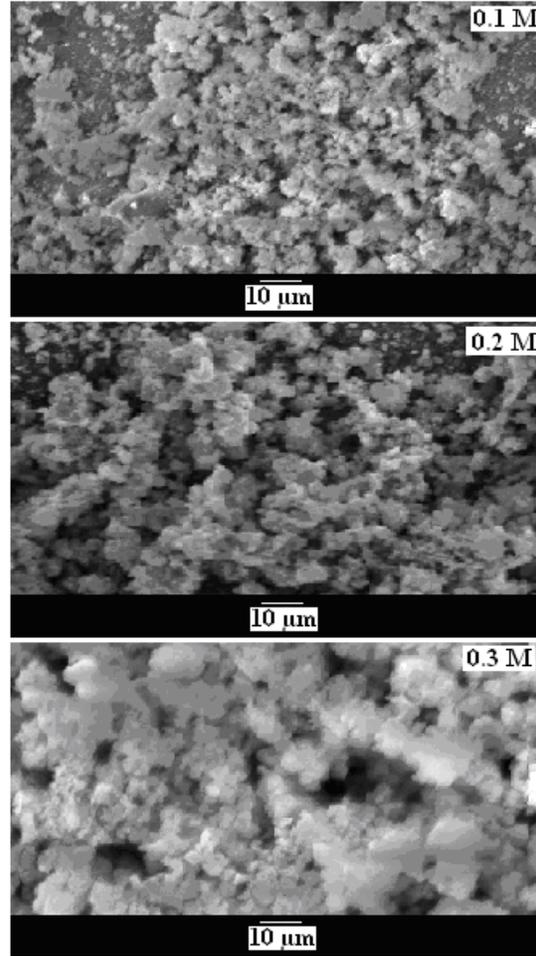Figure 3 shows the SEM images of the NiO films coated with different molarities at 350ºC.

Fig 3

Figure 3: .SEM micrographs of NiO thin films coated with different molarities at 350ºC.

The SEM pictures showed that the films are uniform, well adherent and completely devoid of pinholes and cracks. Films with 0.1 M of solution concentration has smooth surface with grains scattered throughout the surface. With 0.2 M of solution, the surface starts to modify and smaller granular

particles of nano size were found uniformly distributed all over the surface. When the solution concentration is increased to 0.3 M, the surface becomes probably filled with the clusters of the larger nano grains. This is due to the increased crystallite size obtained for the films with higher molarity as evident from the XRD results. Thus NiO films with nano sized grains were obtained by this simplified spray technique at lower substrate temperature as compared to the other conventional spray methods which is an added advantage of this technique.

III.4 Optical absorption

Measurements of spectral transmittance and reflectance of the as-deposited samples showed that the films coated with 0.1 M of precursor solution concentration has a maximum transmittance of nearly equal to 80% all over the spectral range 300 - 1100 nm as shown in Fig 4.
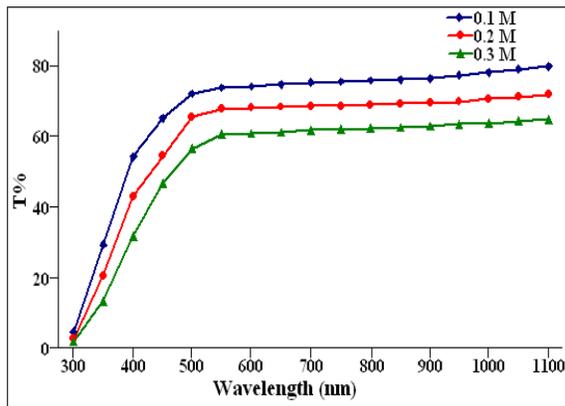

Fig 4

Figure 4: Optical transmittance of NiO thin films coated with different molarities at 350ºC.

The transmittance decreases with increase in the molarity of the solution. This is attributed to the increase in the film thickness, with subsequent increase in absorption. In the thicker films, the onset of the absorption edge became less sharp, this is due to the fact that, as the concentration increases, bigger clusters are deposited; and the scattered radiation became remarkable due to the surface roughness. The absorption coefficient α was obtained using the relation:

$$\alpha(\lambda) = \frac{10^{4}}{t} \log_{10}\left[\frac{(1-R(\lambda))^{2}}{T(\lambda)}\right] \qquad (5)$$

where t is the film thickness, $R(\lambda)$ and $T(\lambda)$ are the reflectance and transmittance at the specified wavelength λ. The absorption coefficient is found to be of the order of 10^{6} cm^{-1}. The optical absorption coefficient is related with the energy band gap and it is given by the equation:

$$\alpha = A(h\gamma - E_{g})^{n} \qquad (6)$$

where A is a constant, $h\gamma$ is the incident photon energy, and n depends on the nature of band transition; n = 1/2 or 3/2 for direct allowed and direct forbidden transitions, and n = 2 or 3 for indirect allowed and indirect forbidden transitions and E_{g} is the optical band gap.

Apparently the plot of $(\alpha h\gamma)^{2}$ or $(\alpha h\gamma)^{1/2}$ against $h\gamma$ provides the nature and E_{g} value of the coated film. The indirect band gap energy is obtained by extrapolating the linear portion of $(\alpha h\gamma)^{2}$ versus $h\gamma$ to energy axis at $\alpha = 0$ as shown in Fig 5.
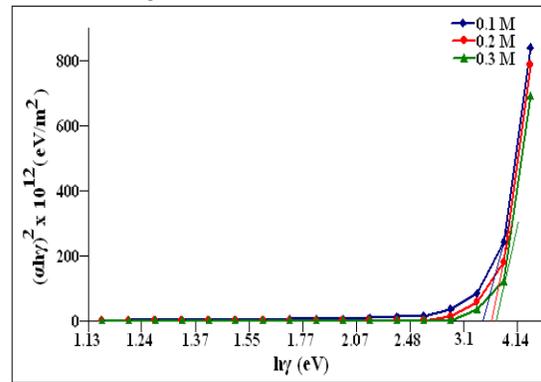

Fig 5

Figure 5: Plot of $(\alpha h\upsilon)^{2}$ versus $h\upsilon$ for as deposited NiO films coated at 350ºC.

The indirect band gap energy for the NiO film varies from 3.62 eV to 3.47 eV as the solution concentration varies from 0.1 M to 0.3 M. The band gap value decreases as the solution concentration increases, which might be due to increased thickness obtained for the films with higher molarity. This decrease in the band gap can be related to the structural modification of the films with higher molarity. It can be supposed that more

oxygen atoms from the sprayed deposition can replace either substitutional or interstitial sites in the NiO lattice creating the structural deformation. The introduction of more oxygen atoms creates some additional energy levels in the NiO band gap close to the valence band edge, with a subsequent reduction of the energy associated with indirect transition of the films coated with higher molarity. The values of band gap energy agree with the reported values of band gap [27, 28]. A comparative study with the same previous findings is given in Table 5.

Table 5. A review of some published data on the energy gap and its comparison with the present findings.

Reference	E_g value (eV)	Transition type	Deposition Parameter / Annealing temp	Preparation tech-nique
[6]	3.6	Direct E_g	Annealed at 350º C	Solution growth
[7]	3.25	Direct E_g	Annealed at 380º C	Solution growth
	3.75		Annealed at 550º C	
	4.0		Bulk	
[9]	4.0	In-direct E_g	Bulk	Thermal evaporation
[29]	3.15 to 3.5	In-direct E_g	$T_s = 300$ - 480ºC	Spray pyro-lysis
	2.5 to 3.7	In-direct E_g	Different SND	
Present work	3.62 to 3.47	In-direct E_g	$T_s = 350ºC$ with different solution concentration	Simplified spray technique using perfume atomizer

The extinction coefficient (k) and the refractive index provide the optical properties of the coated NiO thin films. The value of k was obtained using the equation,

$$k = \frac{\alpha\lambda}{4\pi} \tag{7}$$

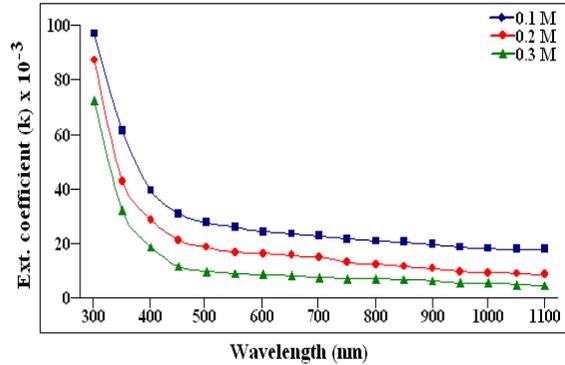The variation in 'k' as a function of wavelength is shown in Fig 6.

Figure 6: Plot of extinction coefficient (k) and wavelength.

From the fig, it is clear that 'k' decreases rapidly with increasing wavelength from 300 to 500 nm and after that the value of 'k' remains constant. The rise and fall in the value of 'k' is directly related to the absorption of light. The lower value of 'k' in the wavelength range 500–1000 nm implies that these films absorb light in this region very easily.

The refractive index has been calculated using the relation

$$n = \left(\frac{1+R}{1-R}\right) + \sqrt{\left(\frac{4R}{(1-R)^2} - k^2\right)} \tag{8}$$

where R is the optical reflectance. The variation of n with wavelength for NiO films coated with different solution concentrations are shown in Fig 7.
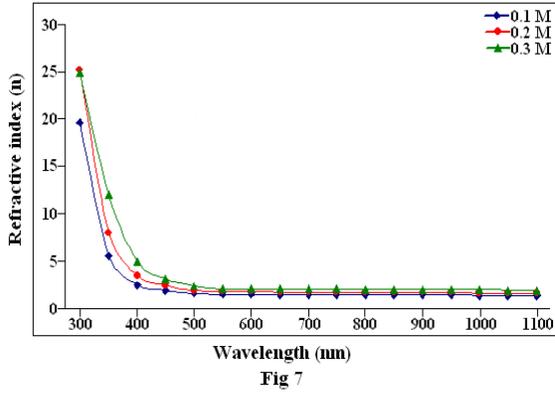
Fig 7

Figure 7: Variation of refractive index (n) with the wavelength of NiO films coated with different molarities.

From the figure, it is clear that the refractive index is nearly constant about 2.31 in the wavelength range 500 – 1000 nm. Beyond the absorption edge region, there is a sharp rise in the refractive index value.

III.5 Electrical properties

Hot probe technique was used to determine the nature of the as-deposited films, which shows current flowing from hot to the cold junction indicating that the films coated are of p-type. The sheet resistance (R_{sh}) and electrical resistivity (ρ) of all the films were observed using four point probe method and the variation in R_{sh} as a function of solution concentration, at different temperatures is shown in Fig 8.
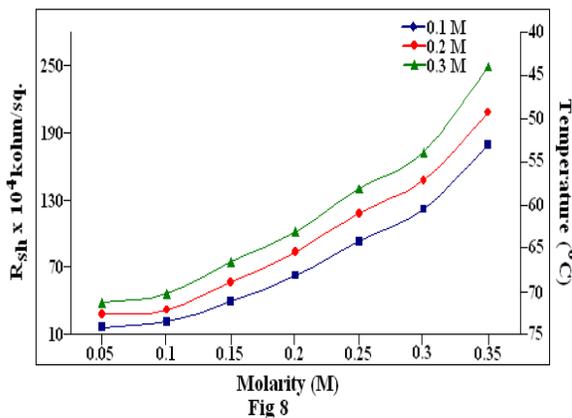

Fig 8

Figure 8: Variation of sheet resistance with solution concentration and temperature.

It is found that the sheet resistance decreases with increases in temperature indicating the semi conducting nature of these films. It is observed that the sheet resistance increases with solution concentration. The increase in sheet resistance with concentration may be due to the increase in the thickness of the film coated with higher concentration. The increase in solution concentration leads to larger grain size as evident from the XRD results which evidently increase the sheet resistance of the films with higher molarity concentration. Films coated with 0.1 M have more resistivity and it decreases as the solution concentration increases. This increase in resistivity for the films coated with lower solution concentration may be due to the decrease in electron concentration. At higher solution concentration, NiO films with improved crystallinity is obtained, which in turn may reduce grain boundary scattering and transmittance with a consequent reduction in the resistivity of the films with higher molarity.

Film thickness affects the resistivity of thin film and its other properties. As the film thickness increases, the resistivity decreases. This behaviour may be due to increase of crystallite size and carrier concentration. Films coated with lower solution concentration had poor crystallinity with increased resistivity, which was primarily due to the decrease in carrier concentration. The poor crystallinity of these films may be due to the presence of a few atomic layers of disordered atoms [**30**]. Since the atoms in the poor crystallized area were disordered, there were a large number of defects due to incomplete atomic bonding, which reduces the carrier concentration of these films.

From the resistance values recorded at different temperatures, the temperature coefficient of resistance (TCR) of the films is evaluated. The variation in TCR as a function of solution concentration is given in Fig 9.
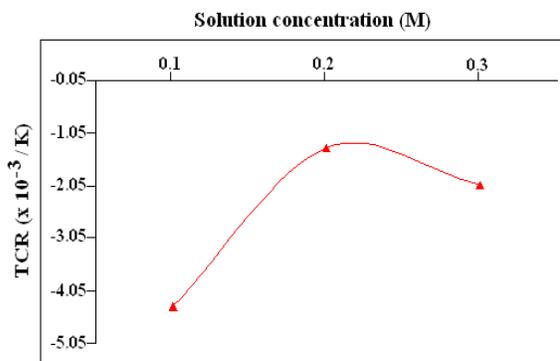
927

Figure 9: Variation of TCR with solution concentration.

The figure reveals that the magnitude of TCR is smaller (-1.34×10^{-3} / K) for the film coated with 0.2 M, indicating that films coated with 0.2 M have heat resistant property which is one of the desirable qualities for solar cell TCO layers. The magnitude of the TCR of the films with 0.2 M is remarkably less indicating that the films coated using this simplified spray technique have higher thermal stability.

IV. CONCLUSION

Nickel oxide thin films with different molarities of nickel chloride have been prepared onto glass substrates kept at 350ºC by employing an inexpensive simplified spray technique using a perfume atomizer. XRD studies show that all the films are polycrystalline in nature with cubic structure having preferential orientation along the (1 1 1) plane. Micro structural parameters have been calculated for all the samples. SEM images showed nano sized grains obtained in this work. Optical absorption studies showed that film coated with 0.1 M of solution has maximum transmittance of 80%. Grain size increases from 15.9 nm to 42.3 nm as the solution concentration increases. The value of absorption coefficient for all the samples is in the order of 10^6 cm^{-1} with indirect band transition. The band gap energy decreases with the increase in solution concentration. The high transmittance and band gap values obtained are well suited for optoelectronic applications. Optical constants such as refractive index, extinction coefficient have been evaluated using the reflectance and absorbance data. The magnitude of TCR obtained for the film coated with 0.2 M is very small indicating the better thermal stability of the films obtained in this work. Also the films coated using this spray technique have heat resistant property which is one of the desired qualities for solar cell TCO layers. All the above mentioned properties deposited by this simplified technique were found to be fairly comparable with that of their conventional spray counterparts. Hence this simplified spray technique can be considered as a desirable alternative to conventional spray, for the production of low cost, large area coatings of device quality NiO films.

References

[1]   C.G. Granqvist, "Handbook of Inorganic Electrochromic Materials" Elsevier, New York; 1995.

[2]   I. Hotovy, J. Huran, P. Siciliano, S. Capone, L. Spiess, V. Rehacek, "Thickness influence on gas sensing characteristics of NiO thin films" Sensors and Actuators **B78**, 126 (2001).

[3]   B. Pejova, T. Kocareva, M. Najdoski, I. Grozdanov, "Chemically deposited nanocrystalline NiO thin films for supercapacitor applications", Appl. Surf. Sci. **165**, 271 (2000).

[4]   A.J. Varkey, A.F. Fort, "A solution growth route to

nanocrystalline nickel oxide thin films", Thin Solid Films **235**, 47 (1993).

[5] E. Jujii, A. Tomozawa, H. Torii, R. Takayama, "Opto-structural, electrical and electrochromic properties of crystalline nickel oxide thin films prepared by spray pyrolysis", Jpn. J. Appl. Phys. **35** 328 (1996).

[6] H. Sato, T. Minami, S. Takata, T. Jamada, "Transparent conducting p-type NiO thin films prepared by magnetron sputtering", Thin Solid Films **236** 27 (1993).

[7] A. IIda, R. Nishikawa, "Effects of oxygen partial pressure on optical properties of NiO_x thin films" Jpn. J. Appl. Phys. **33**, 3952 (1995).

[8] A.F. Wells: "Structural Inorganic Chemistry", 5th Ed., Clarendon Press, Oxford; 1984, p.358.

[9] P. Lunkenheimer, A. Loidl, C.R. Ottermann, K. Bage, "Correlated barrier hopping in NiO thin films", Phys. Rev. **B 44**; 59278 (1991).

[10] Y. Ushio, A. Ishikawa, T. Niwa, "Degradation of the electrochromic nickel oxide film upon redox cycling", Thin Solid Films **280**, 233 (1996).

[11] S.A. Aly, S.A. Mahmoud, M. Abdel-Rahman, K. Abdel-Hady, "The electrochromic behaviour of nickel oxide films sprayed at different preparative conditions", Egypt. J. Sol. **21,** 59 (1998).

[12] T. Maruyama, S. Arai, "Electrochromic Ni oxide films studied by magnetic measurements", Solar Energy Mater. Solar cells **30** 257 (1993).

[13] I. Bouessay, A. Rougier, P. Poizot, J. Moscovici, A. Michalowicz, J.M. Tarascon, "Electrochromic properties of intercrossing Nickel oxide nanoflakes synthesized by electrochromically anodic deposition", Electrochim. Acta. **50**; 3737 (2005).

[14] A. Agrawal, H.R. Habibi, R.K. Agrawal, J.P. Cronin, D.M. Roberts, R.S. Caron-Popowich, C.M. Lampert, "Electrochromic nickel oxide thin films deposited under different sputtering conditions", Thin Solid Films **221**, 239 (1992).

[15] M. Utriainen, M. Kroger-Laukkanen, L. Niinisto, "Ferromagnetic nano tubes by atomic layer deposition in anodic alumina membranes", Mater. Sci. Eng. **B54**; 98 (1998).

[16] R. Cerc Korosec, P. Bukovec, "Sol-Gel prepared NiO thin films for Electrochromic applications" Thermochim. Acta. **410**, 65 (2004).

[17] P.S. Patil, L.D. Kadam, "Preparation and characterization of spray pyrolysed NiO thin films", Appl. Surf. Sci. **199**, 211 (2002).

[18] M. Chigane, M. Ishikawa, "Enhanced Electrochromic property of Nickel Hydroxide thin films by anodic deposition", J. Electrochem. Soc. **141**; 3439 (1994).

[19] Y. Sawada, C. Kobayashi, S. Seki and H. Funakubo, "Highly conducting Indium tin oxide transparent films fabricated by spray CVD using ethanol solution of indium(III) chloride and tin(II)

chloride", Thin Solid Films **409**, 46 (2002).

[20] T. Fukano and T. Motohiro, "Low temperature growth of highly crystallized fluorine doped tin oxide thin films by intermittent spray pyrolysis deposition", Sol. Energy Mater. Sol. Cells **82**, 567 (2004).

[21] Joint Committee on powder diffraction standards International centre for diffraction data JCPDS 04 – 0835.

[22] J. Park, K. Ahn, Y. Nah and H. Shim, Y. Sung, "Optical properties of chemical bath deposited nickel oxide thin films", J. Sol-Gel Sci. and Tech. **31**, 323 (2004).

[23] F. Atay, S. Kose, V. Bilgin and I. Akyuz, "Electrical, optical and structural properties of NiS thin films", Turk. J. Phys. **27**,285 (2003).

[24] ICDD Card No. 47 – 1049.

[25] S.A. Mahmoud, A.A. Akl, H. Kamal, K. Abdel-Hady, "Structural and Optical Dispersion characterization of sprayed NiO thin films", Physica **B 311**, 366 (2002).

[26] B.A. Reguig, M. Regragui, M. Morsli, A. Khelil, M. Addou, J.C. Bernede, "Properties of NiO thin films deposited by intermittent spray pyrolysis", Solar Energy Materials & Solar Cells **90**, 1381 (2006).

[27] I. Hamberg, C.G. Granqvist, "Optical and electrical properties of radio frequency sputtered tin oxide films doped with oxygen vacancies, F, Sb, Mo", J. Appl. Phys. **60**, R 123 (1980).

[28] Z.M. Jarzebski, "Oxide Semiconductors", Pergamon Press, Poland, 1973.

[29] P. Puspharajah, S. Radhakrishna, "Characterization of sputtered NiO thin films", J. Mater. Sci. **32**, 3001 (1997).

[30] J.Y.W. Seto, "The electrical properties of polycrystalline silicon films", J. Appl. Phys. **46**, 5247 (1975).