RESEARCH ARTICLE

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Influence of Annealing on Physical, Physiological and Electric Properties of Mono Nickel oxide Thick Films Prepared by using Screen-Printing Technique

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ABSTRACT

To study changes in physical, physiological and electrical properties of AR grade Nickel monoxide (NiO), thick films of NiO were fabricated on a glass substrate and annealed at 250 ^{0}C - 400 ^{0}C. Using characterization techniques, such as XRD, SEM-EDS and static gas sensing system, the structure of the film was found to be polycrystalline with a cubic structure and chemical composition study confirmed its non- stoichiometric nature. Half bridge method is used for measurement of D.C. resistance of thick films in air atmosphere at 30 ^{0}C to 350 ^{0}C. The prepared thick films of NiO nanoparticles were analysed for electrical properties and it ascertained that they are semiconducting in nature. The TCR, activation energy as well as film resistivity were measured at selected annealing temperatures. The D.C electrical conductivity results obtained from electrical properties at room temperature is $0.086 \times 10^{-4} (\Omega m)^{-1}$. The crystallite size changes from 8.20 nm to 8.54 nm for strong predominant orientation (200) with increase in annealing temperature. Study of correlation between annealing temperature and electrical resistivity showed that there is decrease in resistance with increase in temperature.

Keywords: XRD, TCR, Nickel Oxide thick films, D.C electrical conductivity, activation energy.

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INTRODUCTION

In current era, nanocrystalline transition metal oxides (TMO) have attracted extensive interest because of their various different potential applications. Out of these, the most attractive material is nickel oxide (NiO). NiO is formed of nickel metal and nonmetal oxygen. It has a cubic structure with crystal lattice constant (a= 0.04816 A.U.) [1]-[4] and it is the most widely used because of its chemical stability. The most chemically stable metal oxide that is NiO due to its low cost is found to have wide applications in various fields namely as a catalyst, TCO, photodetectors, electrochromic, a gas sensor, photovoltaic devices, electrochemical supercapacitors, photo- solar cells and many opto- electronic devices [5]-[7]. As one of the components NiO was used in the Nickel-Iron (Ni-Fe) battery (Edison Battery), and fuel cells also.

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Greater surface area-to-volume ratios, high dispersion rates, less porosity, large photo-absorption, and little heat capacities were NiO nanoparticles characteristics. Out of these, unique characteristics of NiO nanoparticles which make it feasible and cost-

effective surfaces convenient for several applications are hydrogen storage photocatalytic degradation of organic dyes, pollutants from effluent as well as antimicrobial activity. The crystalline structure of NiO nanoparticles reveals that it has NaCl-type cubic as well as Bunsenite is a p- type semiconductor metal oxide with wide bandgap varying from 3.63 to 4.0 eV [8]. It can show different properties such as optical, structural and electrical properties etc. on doping with external elements. The particle size reduction to nano meter scale results interesting properties in compared with their bulk properties [9]. Due to structural defect the nonstoichiometric nickel oxide also exhibits properties of p-type semiconductor [10]. NiO nanoparticles have been characterized and synthesized by techniques SEM, EDAX, XRD, static gas sensing system. When material is to be selected and process is to decide to prepare a device then the material properties like electrical, optical, magnetic, thermal and mechanical play a significant role. Now a day's different applications of Nickel oxide (NiO) are observed in various fields mainly semiconductors, capacitor–inductor devices, tuned circuits, batteries, supercapacitors, electrochromic and chemical or temperature sensing devices, transparent heat mirrors thermistors and varistors and so on.

Various techniques such as thermal evaporation, vapor or electrochemical deposition, sol-gel sputtering, screen printing technique, chemical solution deposition can be used to prepare nickel oxide films. Several efforts have been made to get films with the desirable physical and chemical properties as they have several benefits which depends on the application interest. Out of various methods for film deposition screen printing technique is more attractive and viable for mass production processes as it is relatively, simple, inexpensive and has potential application for very large area deposition. The aim of present work is to evaluate the firing effect on physical and electrical properties of Bunsenite NiO thick ûlms deposited by simple and universal screen-printing technique. The NiO thick films were heated on the glass substrates at a different annealing temperature. The effect of annealing on physical, physiological and electrical properties was investigated in the experimental outcomes and discussion section in detail.[11]. This present study will also give guidelines for the preparation of thick films of other transition metal oxides and respective characterization.

EXPERIMENTAL METHOD AND MEASUREMENTS

AR grade Nickel Oxide nano powders were commercially available bought from Nano research lab, Haryana used without further purification and utilized without any additional refinement. Other than this, chemicals such as acetone, Butyl Carbitol Acetate (BCA), white coloured ethyl cellulose etc. required to prepare thick films were purchased from Modern Lab Nashik.

The structure of NiO was verified by measured X-ray spectra diffraction (XRD). Bruker D8 advance diffractometer, Germany using Cu Kα with wavelength 0.154nm radiation functioned at 40 K V and 40 mA in operating the range (2Ÿ) from 20° and 80°, diffraction pattern of the specimen were recorded. SEM-JEOL-JSM 6360 Model with OSFORD EDAX attachment was used to analyse chemical structure and surface physiology. For electrical characterization, static gas sensing system is used.

Thick film preparation of NiO NPs

Universal Screen-Printing Technique (SPT) was used to prepare Nickel oxide (NiO) thick film unique sensor. It is a fundamental layer deposition and patterning process in thick film technology. The conversion of selected powdered NPs of NiO into paste form is done. To keep ratio of the inorganic to organic materials ratio at 70:30, screen-printing method was used to prepare thick films. Nanoparticles of NiO constitute the inorganic part while 8% ethyl cellulose (EC) and 92% B.C.A constitute organic part. Metal oxide and binders taken in fixed proportion are mixed together in mortar and pestle arrangement, crushed continuously for about 40 minutes. The achievement of proper thixotropic properties of the paste was done by adding BCA into crushed powder of Nickel oxide and binders drop by drop. Such a thick solution is applied over glass substrate. The prepared and well mixed paste was applied on previously cut-glass films with 1.5 X 2 cm dimensions. The coated films were initially air dried for 20 minutes and then dried for 30 minutes using IR radiation. For calcination process at numerous temperature 250^{0}C,300^{0}C,350^{0}Cand 400^{0}C the prepared nickel oxide films was kept in muffle furnace for about 120 minutes. One film taken is unannealed that means annealed at room temperature. On the next day the annealed thick films were taken away from furnace for further work [12,13]. The prepared thick films were ready for selected characterization [14,15].

Thick Films Characterization

The prepared samples were characterized by XRD, SEM with EDAX and electrical characterization.

Measurement of film thickness - Thickness of films was calculated by using weight difference method as given in equation (1). After calculations thickness was observed to be in the range of micrometre. As per these calculations a thickness value of the prepared thick film sensor observed is in the range from 20 to 36 micrometre.

$$t = \frac{\text{difference in weight}}{\text{Area} * \text{density}}$$

$$t = \Delta w / A * \rho \quad (1)$$

Here, Δw is difference in weight of the film sensor after and before covering,

ρ is its density (Nickel oxide) = 6.67 gm/cm^3

A is film area (length*breadth)

Measurement of thickness of the specimen with respect to annealing temperature was mentioned in table II.

Structural Characterization of Prepared Thick Film

Using X-ray diffraction analysis in the operating range from 20-80^0 with Cu-Kα having λ=1.542A.U., physical properties of prepared NiO films were examined. Surface (morphology) physiology was carried using SEM. Using energy dispersive X ray spectrometer (EDAX), constitution (composition) of prepared NiO thick film specimen was determined.

The crystal size was calculated using Debye-Scherer's formula [16]and is as follows,

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad (2)$$

λ = 1.542 A^o, wavelength of radiations,
β = FWMH (full width at half maximum)
D = crystallite size.

Morphology of NiO thick films

By making use of field emission scanning electron microscopy (FESEM), surface structure of NiO thick films was explored.

Electrical Characterization

The value of D.C. resistance of prepared thick film specimen was determined by using half bridge method as temperature dependent [17,18]. By connecting a load resistor R_L in series with thick film sensor and by applying a fixed D.C. voltage (V_{app}) of approximately 30V to the circuit the setting of the film was done at constant surrounding temperature. Using digital multimeter (DMM) across load resistor R_L, output voltage (Vo)was measured and hence resistance of thick film specimen R_S was calculated. To record the operating temperature chromel-alumel (Cr-Al) thermocouple was used as Digital temperature controller system. The calculation of sample resistance (Rs) of thick film sensor was done by using relation,

$$R_s = R_L\left(\frac{V_{app}}{V_0} - 1\right) \quad (3)$$

Where symbols represent the quantities mentioned above.

By using prepared film dimensions namely breadth, thickness and length, value of film resistivity can be determined.

The film resistance of undoped NiO film sensors was dictated from following condition as mentioned by (4)

$$\rho = \frac{Rbt}{l} \quad (4)$$

Where symbol denotes

ρ = Resistivity of prepared film sensors,

R = resistance at temperature, T

b = breadth of film sample,

t = film thickness

l = length of the sensor film.

The temperature effect on resistance was studied to determine temperature coefficient of resistance (T.C.R.) and it is calculated as

$$T.C.R. = \frac{1}{R_0} = \frac{\Delta R}{\Delta R} \quad /^0 K \quad (5)$$

Where ΔR represents change in resistance between temperature T_1 and T_2,

Ro= initial resistance of film sample

ΔT is temperature difference between T_1 and T_2

Using Arrhenius plot of thick film sensor, activation energy (ΔE) of thick film sensor was calculated and is given by expression

$$R = R_O\, e^{-\Delta E/kT} \quad (6)$$

Where, k= Boltzmann constant &T= absolute temperature.

A plot of electrical resistance (R) versus 1/T (inverse of temperature) can be used to calculate activation (excitation) energy (ΔE), in a given temperature slot. By varying temperature from 30 ^{0}C to 350 ^{0}C, activation energy (ΔE) and T.C.R. were evaluated.

EXRERIMENTAL OUTCOMES AND IT'S ANALYSIS

Structural Parameters

Figure 1 shows X-ray diffraction patterns obtained for NiO thick films fired at 400^{0}C [9]. It was observed in all temperature cases peaks showing the presence of NiO well coincide with reported JCPDS (No.47-1049) data available. As annealing temperature increases the width of XRD peaks decreases. Grain size of thick film is depending on annealing temperature and its XRD analysis shows that all films are arbitrarily oriented grains of polycrystalline nature. Also, at higher temperatures size of grain increases with simultaneous decrease in surface area. Some of the key properties for a sensing film such as the structural stability, porosity and high surface to volume ratio and so on, are basically used in the field of chemical sensors [19]. Here prepared NiO thick film is fired in the range of 250 to 400^{0}C. Using XRD Pattern its crystalline size was calculated and observed as 8.20935 nm at 250 ^{0}C and at 400^{0}C was 8.54165nm using Scherrer formula for predominant orientation (200).

Crystalloid parameters: Using Debye-Scherer's formula, crystallite size of NiO thick films specimen at firing temperatures was calculated by considering XRD pattern. [20].

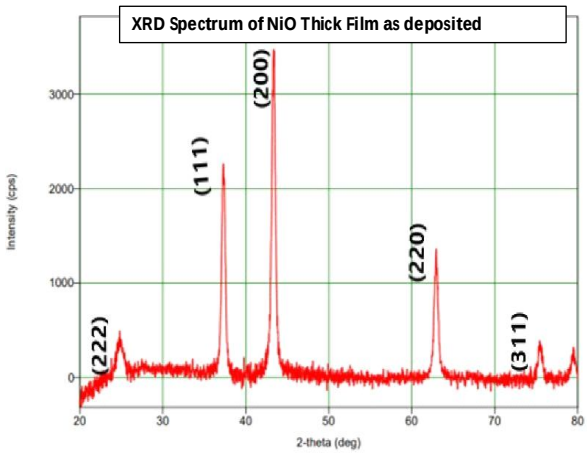

Figure 1: XRD pattern at firing temperatures(400^{o}C)

Morphology (Physiology) of NiO thick films

With the help of field emission scanning electron microscopy (FESEM), surface structure of Nickel oxide (NiO) thick films was revealed. Figure 2 shows the SEM images NiO thick films at two different annealing temperatures. It is cleared from Figure that NiO thick films are constituted of aggregates of grains in spherical shape [11]. Some singular spherical grains have also been observed in the morphology whose size range 181nm to 233nm. The SEM micrographs reveals that the samples have good dispersibility.

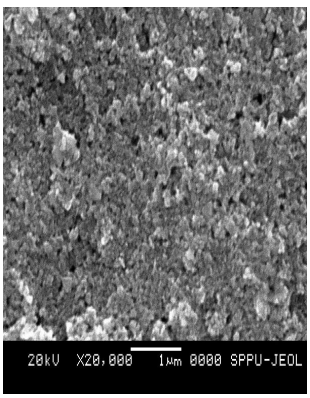

Figure 2a: SEM images of NiO thick films when film is unannealed

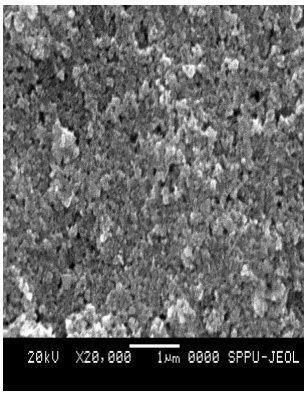

Figure 2b: SEM images of NiO thick films: film is annealed at 400^{O}C

Elemental Composition

With increasing annealing temperature, excess oxygen is removed and so the weight percentage of Nickel (Ni) is increases while that of mass percentage of Oxygen decreases. It was seen in the table-1; Table-1 shows quantitative elemental analysis of pure NiO thick films [13].

Table-1: Elemental Quantitative Analysis of Pure NIO Thick Films using SEM-EDAX.

Sample Annealed Temperature	Elements				Ni/O Ratio
	Ni		O		
	At. wt.%	At. Mass %	At. wt.%	At. Mass %	
As deposited	58.64	72.13	41.36	27.87	1.41770
250^0 C	60.38	29.352	39.62	70.650	1.5239
300^0 C	60.41	29.37	39.513	70.63	1.52589
350^0 C	60.431	29.38	39.57	70.621	1.5271
400^0 C	60.32	29.37	39.42	70.42	1.5302

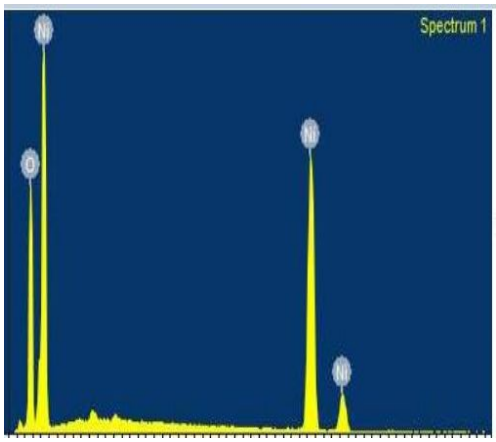

Figure 3: EDAX of NiO Thick film at 400 °C

The two peaks in EDAX spectra indicates that only Nickel & Oxygen are present and impurities are absent in specimen. Such a proportion observed to be the oxygen deficient and leads to conducting nature of NiO [21]-[22]. Thick NiO films were fired at 400^{0}C; also, it observed increase in Ni/O ratio. So, the optimized firing temperature 400^{0}C was selected for further studies of NiO thick films.

Electrical Characterization

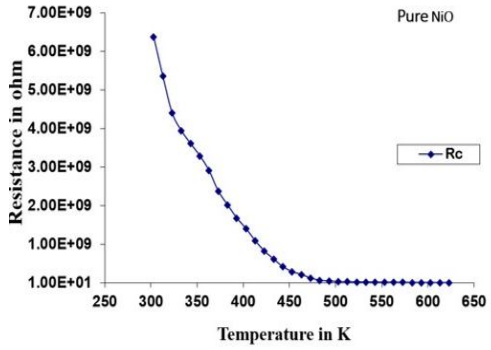

Fig. 4(a): Plot of resistance against temperature for pure NiO thick films at 400^{0}C

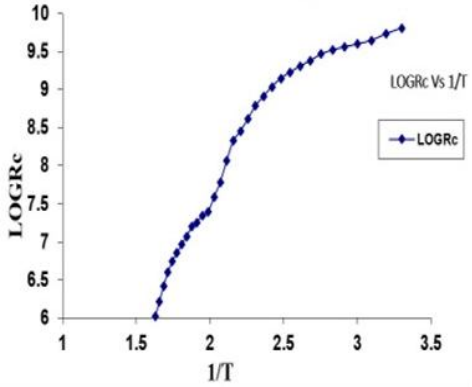

Fig. 4(b): Plot of logR against1/T NiO thick films annealed at 400^{0}C for activation energy

Table-2: Electrical Parameters Obtained For Pure NiO Thick Films

Sample Name	Sample No.	Resistance(?)	Resistivity(? .m)	Thickness (μm)	TCR / k	Activation Energy(eV)	
						At LowTemp x10^{-4}	At High Temp x10^{-4}
Pure NiO	1(unannealed.)	11528461538	11.528x10^4	20	-0.01408	2.3644	5.48092
	2(250^{0}C)	9667419355	17.40 x10^4	36	-0.012564	1.60113	3.8202
	3(300^{0}C)	8098108108	14.17 x10^4	35	-0.53822	1.5788	5.77786
	4(350^{0}C)	6656666667	11.31 x10^4	34	-0.01267	2.38511	9.3850
	5(400^{0}C)	6372978723	11.15 x10^4	35	-0.00051	0.9577	12.09

From observation table it is concluded that resistivity decreases from 17.40 x10^4 to 11.15 x10^4 Ωm with increase in annealing temperature. At low operating temperature, a fall in value of film resistivity and activation energy was observed; also grain size enlarges with increase in annealing temperature. TCR increases with increase in annealing temperature [11]as represented in Table-2. These results lead to conclusion that increase in degree of crystallinity with firing temperatures.

CONCLUSION

Using simple, cost-effective screen-printing technique nickel monoxide thick films specimen with different thickness observed in micrometres have been successfully deposited on glass substrate. The structural(physical) and electrical properties have been systematically investigated for Nickel oxide thick films. The unannealed films prepared are annealed in the temperature range 250^{0}C to 400^{0}C. The polycrystalline nature NiO thick ûlms was confirmed by the XRD analysis. The crystallinity and physiological properties are directly proportional to thickness of the prepared NiO thick films. The average size of the crystal was determined by Debye's Scherrer equation for strong concentrated reflection (200) at $2\theta = 43.43°$ is 8.532 nm. From EDAX spectra, it can be concluded that compositions of Nickel (Ni) and Oxygen is of variable in nature. As film resistivity of prepared NiO thick films is observed to decreases with increase in annealing temperature. Hence NiO thick film specimen are of semiconductor nature. However further investigation and optimization still need to be done for doped NiO thick films.

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REFERENCES

[1] M.A. Abbasi, Z.H. Ibupoto, A. Khan, O. Nur, M. Wallander, Mater. Lett. 108, (2013)152. M.D. Irwin, D.B. Buchholz, A.W. Hains, R.P.H. Chang, T.J. Marks, Proceedings of the National Academy of Sciences, art. No 0711990105, (2008)105.

[2] J. Kim, J.-H. Yun, Y.C. Park, W.A. Anderson, Mater. Lett. 75, (2012) 99.

[3] M.-J. Park, J.-Y. Jung, S.-M. Shin, J.-W. Song, Y.-H. Nam, D.-H. Kim, Thin Solid Films 599, (2016) 54.

[4] K.C. Wang, P.S. Shen, M.H. Li, S. Chen, M.W. Lin, P. Chen, ACS Appl. Mater. Interfaces 6(15), (2014)11581.

[5] J.H. Yun, J. Kim, Y.C. Park, S.J. Moon, W.A. Anderson, Thin Solid Films 547, (2013) 17.

[6] S. Ahn, A.H. Tuan, S. Kim, C. Park, C. Shin, Y.J. Lee, Mater. Lett. 132, (2014) 06.

[7] D. Zaouk, Y. Zaatar, R. Asmar, Microelectron. J. 37, (2006) 5.

[8] A.A. Al-Ghamdi, W.E. Mahmoud.J. Yaghmour, F.M. AlMarzouki, J. Alloy. Compd. 486, (2009) 1

[9] M. Ghougali, O. Belahssen, A. Chala1, "Structural, Optical and Electrical Properties of NiO Nanostructure Thin Film" Vol. 8 No 4(2), (4pp) (2016)040591-4

[10] H.-L. Chen, Y.-M. Lu, and W.-S. Hwang, "Characterization of sputtered NiO thin films," Surface and Coatings Technology, vol. 198, no. 1–3, pp. (2005) 138–142.

[11] Patil et. al., "Synthesis, characterization and gas sensing performance of SnO2 thin Films prepared by spray pyrolysis", Bull Mater Sci, 2011; 34(1): 1–9.

[12] Hazaa S Q, et. al. "Undoped and Cobalt Doped ZnO Thin Films Ethanol Gas Sensors", Int Journal of Latest Res in Eng and Tech, 2016; 02 (08):01-05.

[13] Mirzaei A et. al., "Fe2O3/Co3O4 composite nanoparticle ethanol sensor", Kor Journal of Physical Society, 2016; 69 (3),373–8.

[14] U.J. Tupe, M. S. Zambare, A.V. Patil and P. B. Koli, "The Binary Oxide NiO-CuO Nanocomposite Based Thick Film Sensor for the Acute Detection of Hydrogen Sulphide Gas Vapours", ISSN: 0973-3469, Vol.17, No. (3) 2020, Pg. 260-269.

[15] L. Gao, Q. Li, Z. Song, J. Wang, Preparation of nanoscale Titania thick film and its oxygen Sensitivity Sensors and Actuators B, 71, 2000, pp. 179-183.

[16] B. Ramasubba Reddy, G. S. Harish, Ch. Seshendra Reddy, P. Sreedhara Reddy "'Synthesis and characterization of Cu doped NiO nanoparticles'', IJMER | ISSN: 2249–6645 | www.ijmer.com Vol. 4 (2014) 62-66

[17] S.K. Noukelag, H.E.A. Mohamed, B. Moussa, L.C. Razanamahandry, S.K.O. Ntwampe, C.J. Arendse "Structural and optical investigations of biosynthesized bunsenite NiO nanoparticles (NPs) via an aqueous extract of Rosmarinus officinalis (rosemary) leaves",2214- 7853/ 2020 Elsevier Ltd 1-5

[18] D. Cullity, Elements of X-ray Diffraction, 2nd Edition, Addition Wesley, 1970, p. 102.

[19] I. S. Ahmed Frag, I. K. Battisha, M. M. El_Rafaay, Indian Journal of Pure Appl. Phys. 43 446 (2005).

[20] Hindawi Journal of Nanomaterials Rafia Boubaker Benhaoua, Soufiane "Effect of Precursor Concentration on Structural Optical and Electrical Properties of NiO Thin Films Prepared by Spray Pyrolysis'', Volume 2017, Article ID 5204639, 10 pages.

[21] Zohra Nazir Kayani, Mahek Zaheen Butt Saira Riaz, Shahzad Naseem "Synthesis of NiO nanoparticles by sol-gel technique", Materials Science-Poland, 36(4), 2018, pp. 547-552

[22] Amanulla, A.M.; Shahina, S.K.J.; Sundaram, R.; Magdalane, C.M.; Kaviyarasu, K.; Letsholathebe, D.; Mohamed, S.B.; Kennedy,J; Maaza, M. Antibacterial, optical and humidity sensor studies of _-$CoMoO_4$-Co_3O_4 nanocomposites and its synthesis and characterization. J. Photochem. Photobiol. B 2018, 183, 233–241.