International Journal of Innovative Technology and Exploring Engineering (IJITEE)
ISSN: 2278-3075 (Online), Volume-10 Issue-6, April 2021

Annealing Effect on Structural, Morphological and Electrical Properties by Screen Printed Bunsenite NiO Thick Films.

Ujwala m. Pagar, U. P. Shinde

Abstract: ***Thick films of NiO deposited on glass substrate by screen printing technique. The nano powder of AR grade NiO was used for the preparation of thick films. The X-ray diffraction (XRD), Scanning Electron Microscopy and Electrical Characterization was carried out for unannealed and annealed films. The annealed films were at 250 ^{0} C-400 ^{0} C in a muffle furnace. Using characterisation techniques, the success of the synthesised nanoparticles was confirmed. The x-ray diffraction was used for structural characterization which confirms the polycrystalline nature of the films with cubic structure. From the SEM analysis the films show uniformity, roughness, large crystals and agglomeration of particles. The SEM-EDS analysed morphology and chemical compositions. The correlations between structural and morphological properties are reported. The D.C. resistance of the films was measured by half bridge method in air atmosphere at 30^{O}C to 350^{O}C. From the electrical parameters the NiO films shows semiconducting nature. The TCR, activation energy and sheet resistivity, specific surface area were calculated at different annealing temperatures. The electrical conductivity at room temperature was calculated as*** $4.56 \times 10^{-4}(\Omega \cdot m)^{-1}$.

Keywords: ***NiO, Thick Films, XRD, SEM-EDS, TCR, Activation energy, Electrical conductivity.***

I. INTRODUCTION

Nickel oxide (NiO) is an attractive material due to its chemical stability. It is forming with nickel metal and oxygen element; it has cubic structure with lattice parameter (a= 0.4816 nm) [1-4]. Nickel oxide (NiO) is low-cost material, it is applicable in several application areas such as a catalyst, TCO, photo detectors, gas sensors, photovoltaic devices, electrochemical super capacitors, heat reflectors, photo-electrochemical cell, solar cells and many opto-electronic devices [5-7]. The specialized applications of Nickel (II) oxide (NiO) include, production of alloys, in ceramic industry for making frits, ferrites and porcelain glazes, as a catalyst for chemical and biological sensors. NiO is a basic component in Nickel-iron battery and in fuel cells. The NiO nanoparticles possess distinctive properties such as large surface to volume ratio, low porosity, high dispersion rates, high photo-absorption and low heat capacities. The NiO nano particles exhibit the NaCl-type cubic crystalline structure.

Manuscript received on April 20, 2021.
Revised Manuscript received on April 26, 2021.
Manuscript published on April 30, 2021.
* Correspondence Author
Ujwala M. Pagar*, Department of Physics, H.P.T. Arts and R.Y.K. Science College, Nashik 422005, (M.S.) India.ujwalapagar7@gmail.com
U.P. Shinde, Department of Physics, L.V.H. Arts, Science and Commerce College, Nashik 422005, (M.S.) India .

Bunsenite is an environmentally friendly material having p-type semiconductor metal oxide with a wide band gap ranging from 3.6 to 4.0 eV [8]. After doping with foreign elements in NiO, it shows optical, structural and electrical properties. The reduction of particle size to nanometre scale compared with their bulk properties shows interesting properties [9]. Non stoichiometric nickel oxide is a good p-type semiconductor owing to its defect structure [10]. The applications of Nickel oxide (NiO) found in semiconductors, capacitor–inductor devices, tuned circuits, transparent heat mirrors, thermistors and batteries, micro-super capacitors, and temperature sensing devices. The nickel oxide thin films have been prepared using various techniques including thermal evaporation, spray pyrolysis, chemical vapor deposition, electrochemical deposition, sol-gel sputtering, Screen printing technique, chemical solution deposition etc. All these methods have different advantages depending on their applications. Among these different methods for film deposition, the relatively simple and inexpensive method is screen-printing technique. The effect of annealing on structural, morphological and electrical properties were investigated [11]. The aim of this work is to evaluate the annealing effect on structural, morphological and electrical properties of NiO thick films deposited by simple screen-printing technique.

II. MATERIALS METHOD AND MEASUREMENTS

The commercially available AR grade Nickel Oxide nano powder was used for preparation of thick films. The chemicals other than NiO power required for preparation of thick film are acetone, B.C.A., ethyl cellulose etc purchased from Modern Lab. Nashik etc. The X-ray diffraction (XRD) spectra of the NiO were measured to verify the structure.

The X-ray diffraction patterns of all the samples are recorded for analysis purpose. They were plotted using Bruker D8 advance diffractometer, Germany with CuKα (λ=1.54A.U.) radiations operated at 40 KV and 40 mA in the scanning range of (2θ) between 20° and 80°.

Chemical composition and surface morphology observed using a scanning electron microscope, SEM-JEOLJSM-6360A with OXFORD EDAX attachment. For electrical characterization simple half bridge method was used.

A. Preparation of thick films of Nickel Oxide nanoparticles

The Nickel oxide based thick film sensor was constructed by standard screen-printing technique.

The powder nanoparticle of NiO converted into paste form was used to prepare thick films by screen printing method maintaining the inorganic to organic materials ratio at 70:30. The inorganic part consists of nanoparticles of NiO. The organic part consisted of 8% ethyl cellulose (EC) and 92% butyl carbitol acetate (BCA). All these stoichiometric amounts of metal oxide and binders then mixed into mortar and pestle and crushed continuously for nearly 30 minutes. Then, BCA was mixed into above crushed powder of metal oxide and binders. A solution of BCA which was added drop wise until proper thixotropic properties of the paste achieved. That gel like paste can employed over glass substrate with dimensions 1.5X2 cm. After complete coating of the films, these films were air dried firstly for 20 minutes followed by IR drying for 30 minutes. Finally, the prepared binary oxide film sensor was kept in muffle furnace for calcinations process at various temperatures 250 ^{0}C, 300^{0}C, 350^{0}C, 400^{0}C nearly 2 Hours. On the next day the thick films of nickel oxide was removed from muffle furnace to utilize for further study, such a films are now ready for characterization [12-15].

B. Thickness Measurement of the Films

The thickness of the films calculated by the using the equation (1).

$$t = {\Delta w}/{A * \rho} \qquad (1)$$

Δw = Weight difference of the film sensor after and before coating,

ρ = density of Nickel oxide = 6.67 gm/cm^3

A= area of the film (length*breadth)

After calculations thickness observed in the range from 20 to 36 μm.

III. RESULTS AND DISCUSSION

A. Structural analysis by X-ray diffraction (XRD)

The crystallite size pure NiO thick films are in the range of 8.209-8.549 nm. The X-ray diffraction patterns for the Pure NiO nanoparticles are shown in Figs. 1-5. The XRD pattern of Fig.1-5 reveals the polycrystalline nature for all the films the peaks are indexed as (111), (200), (220), (311) and (222) planes at 2θ values 37.39^o, 43.45^0, 62.98^0, 75.5^0 and 79.49^0 and represents pure Bunsenite face centred cubic (FCC) crystalline structure of nickel oxide. All these diffraction peaks are matched with the standard spectrum JCPDS (No. 47-1049). The predominance of (200) plane clearly shows that the growth of the crystal is such that the a-axis is perpendicular to the surface of the substrate. The lattice parameter of NiO nanoparticles calculated from XRD data, which is in good agreement with the reported data correspond to face centred cubic structure of NiO nanoparticles [16]. The crystal size was calculated according to Debye-Scherrer formula represented below

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

Where wavelength of the radiations λ = 1.54 Å,

β is the full width at half maximum (FWMH),

D = grain size, and θ is the angle obtained from 2θ values corresponding to maximum intensity peak in XRD pattern. From the equation, crystallite size was estimated for sharp intense peak (200) was 8.549 nm.

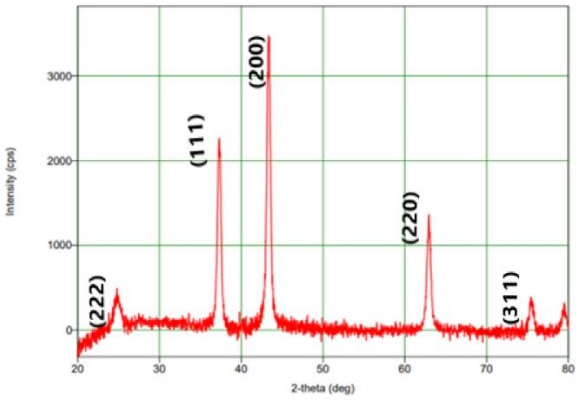

Fig. 1: XRD of unannealed NiO film.

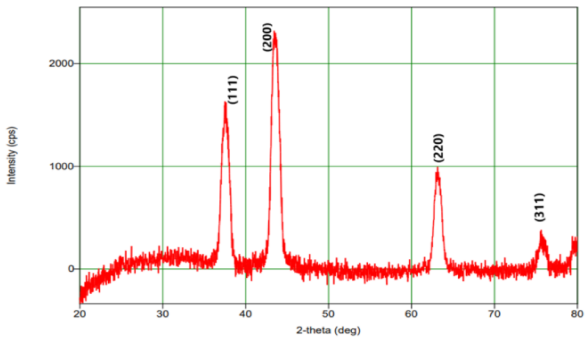

Fig. 2: XRD of NiO film annealed at 250 ^{0}C.

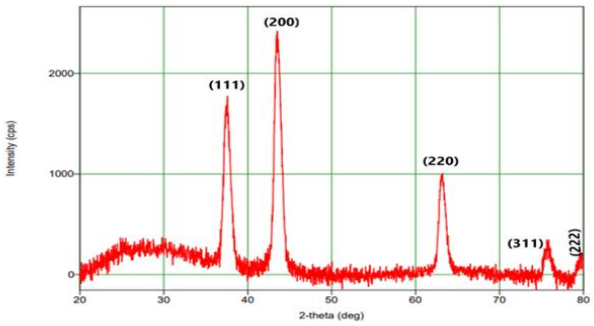

Fig. 3: XRD of NiO film annealed at 300 ^{0}C.

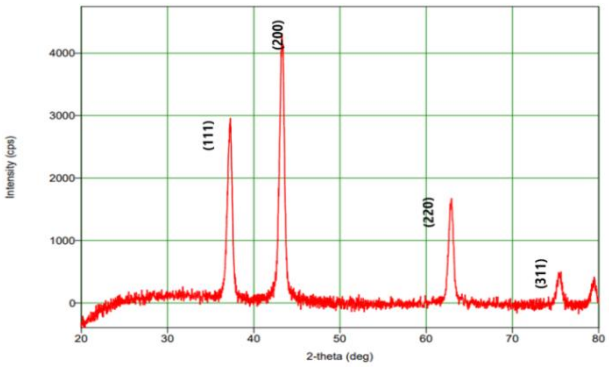

Fig. 4: XRD of NiO film annealed at 350 ^{0}C.

Published By:
Blue Eyes Intelligence Engineering
and Sciences Publication

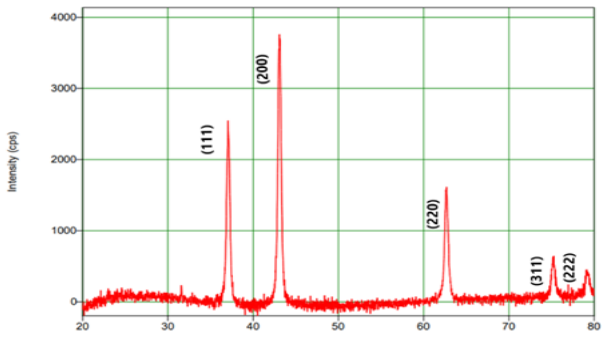

Fig. 5: XRD of NiO film annealed at 400 ^{0}C.

The average crystallite size calculated using the Debye Scherrer equation for most intense reflection (200) at $2\theta = 43.43°$ is 8.532 nm.

The dislocation density and lattice strain were calculated from the diffraction pattern to obtain more information about structural properties. The observed changes of strain are due to point defects and crystallite size. The lattice strain is calculated using Stokes-Wilson equation and to know more on the number of defects in the film, the dislocation density, δ is calculated by using relation mentioned in table I. The induced strain causes reduction in crystallite size and increase in peak broadening. The average micro strain can be seen for NiO thick film sensor is 0.04056 %.

Annealing temperature (^{o}C)	**Dislocation density $\delta = \frac{1}{D^2}$ (lines/m^2)10^{15}**	**Micro Strain $\varepsilon = \frac{\beta cos\theta}{4}, 10^{-3}$**
Unannealed	13.68	4.05299
250	14.83	4.22
300	13.67	4.05
350	13.69	4.053
400	13.70	4.056

Table I: Shows Dislocation density and Micro Strain for different annealing temperatures.

B. SEM (Microstructural) Analysis

The Scanning electron microscopy (SEM-JEOL JSM 6360 Model) images of prepared Nano material NiO thick films are shown in figs. 6-10. The instrumental parameters, accelerating voltage, spot size, and magnification and working distances are indicated on SEM images. The surface characteristics of the prepared films investigated by scanning electron microscopy that shows heterogeneous, porous NiO nanoparticles with varying dimensions. The appearances of some particles are in spherical shape. We can observe that the particles are highly agglomerated and they are essentially cluster of nanoparticles.

The surface morphology of NiO thick films of figs. 6-10 show polycrystalline nature with number of voids (pores) distributed on the surface of film, basically due to evaporation of organic binder during firing the films. The average particle size is different at different temperatures. It is maximum when film is unannealed. The average particle size is 175.8 nm. Surface area decreases with increase in annealing temperature and is a minimum for unannealed film as shown in table II. Surface of NiO thick films are cubical, hexagonal grains, so such a film can adsorb more atmospheric oxygen due to more exposed surface area of the film. Highly porous film shows high sensitivity.

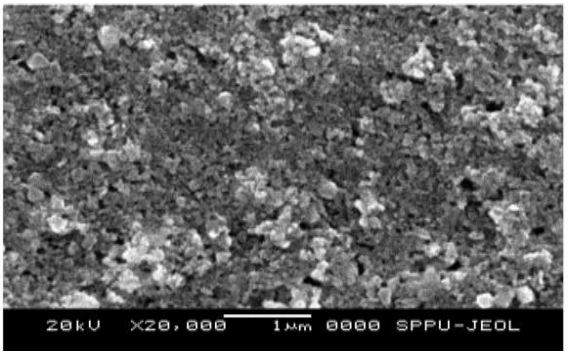

Fig. 6: SEM of unannealed NiO thick film.

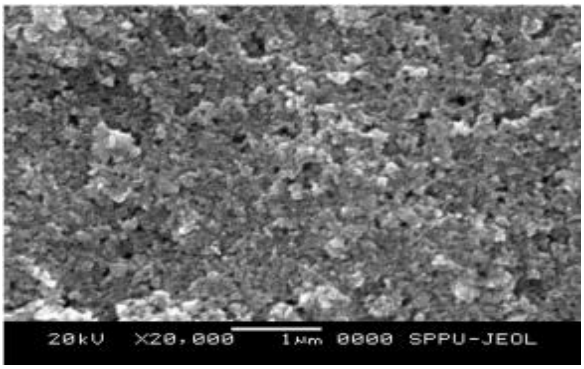

Fig. 7: SEM of NiO annealed at 250 ^{0}C.

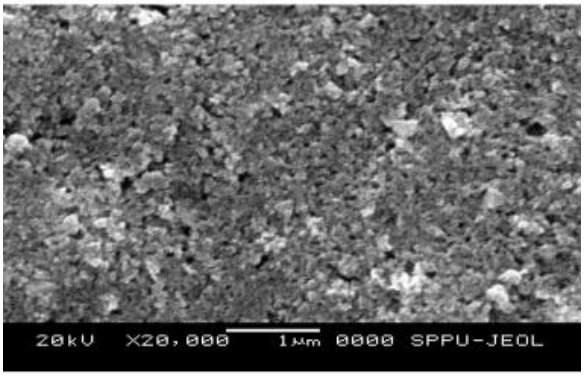

Fig. 8: SEM of NiO annealed at 300 ^{0}C.

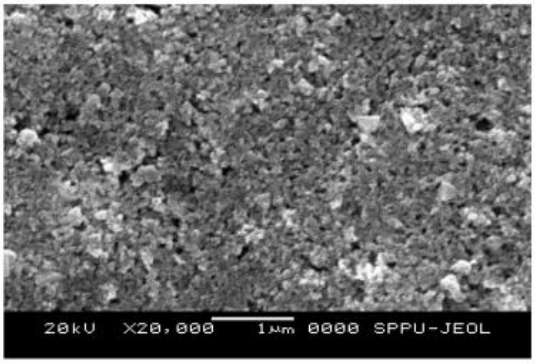

Fig. 9: SEM of NiO annealed at 350 ^{0}C.

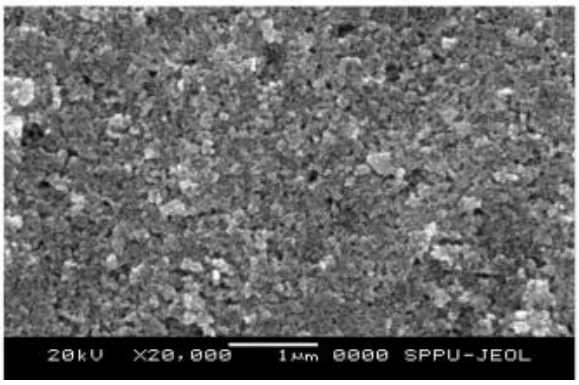

Fig. 10: SEM of NiO annealed at 400 ^{0}C.

Annealing temperature (^{0}C)	Mean Particle size (nm)	Spherical grain diameter 'd ' (nm)	Specific surface area $S_w = \frac{6}{\rho d}$ (m^2/gm)
Unannealed	215.42	130	6.9196
250	167	102	8.8191
300	168.4	114	7.8907
350	169	118.66	7.5809
400	198.8	121.5	7.4037

Table II: Mean particle size, grain diameter and Surface area at various annealing temperatures.

C. EDS Analysis

The composition of grown NiO nanoparticles was determined using the spectra obtained by energy dispersive analysis of X-rays (EDAX). The weight percentage and atomic percentage of nickel oxide nanoparticles are shown in table III. This reveals that synthesized nanoparticles are non-stoichiometric. In nickel oxide this nonstoichiometric is accompanied by colour change, with the stoichiometrically correct NiO being green and non-stoichiometric NiO being black.

Fig.11 Shows Elemental composition at 250 ^{0}C ,300 ^{0}C, 350 ^{0}C ,400 ^{0}C and unannealed NiO thick films.

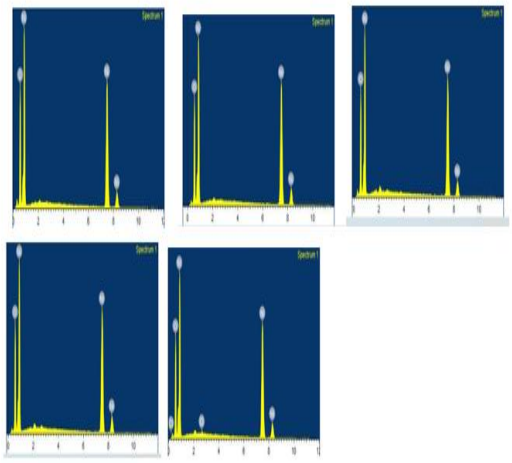

Fig. 11: EDAX results of NiO nanoparticles

The weight percentage of Nickel is increased with annealing temperature and mass percentage of oxygen decreases with increasing annealing temperature due to release of excess oxygen. Table III shows quantitative elemental analysis of NiO.

Sample Annealed Temperature	Elements				Ni/O Ratio
	Ni		O		
	At. wt.%	*At. Mass %*	*At. wt.%*	*At. Mass %*	
Unannealed	58.64	72.13	41.36	27.87	1.4177
250^0 C	60.38	29.35	39.62	70.65	1.5239
300^0 C	60.41	29.37	39.51	70.63	1.5258
350^0 C	60.43	29.38	39.57	70.62	1.5271
400^0 C	60.52	29.37	39.42	70.42	1.5302

Table III: Atomic % elemental composition of Pure NiO thick films as measured by EDS

Crystallinity

Crystallinity index I_{cry} can be calculated through comparison of crystallite size obtained from XRD and that obtained by SEM.

$I_{cry.} = \frac{D_p}{D}$, D_p is particle size from SEM, D by XRD using Debye Scherrer Formula

When I cry is close to 1, it is assumed the crystallites represents mono crystalline units. Much larger value of Icry means the particles are of polycrystalline type. From XRD and SEM, I cry is 20.604 for NiO thick films so prepared thick films shows polycrystalline type.

D. Electrical characterization

The DC resistance of NiO thick films was measured by using half bridge method as a function of temperature described [17].

The resistivity of each film was calculated by [18].

$$\rho = R\ b\ d\ /\ l \qquad (3)$$

where,
ρ = Resistivity of prepared film sensors,
R = resistance at normal temperature
b = breadth of film,
d = thickness of the sensor film
l = length of the sensor film.

Activation energy (ΔE) of thick films was calculated by Arrhenius plot using the relation

$$R=R_0 e^{-\Delta E/kT} \qquad (4)$$

Where, k= Boltzmann constant
T= absolute temperature.

Published By:
Blue Eyes Intelligence Engineering
and Sciences Publication

For the determination of activation energy, the variation of electrical resistance (R) as a function of inverse temperature. From the observed data in the temperature range 30^0C to 350^0C. Resistivity decreases 2190.4 to 1019.67 Ωm with increase in annealing temperature. Activation energy increases with change in annealing temperature. Resistivity and activation energy at low temperature decreases whereas grain size increases with increasing annealing temperature. These results may be assigned to increase in degree of crystallinity with annealing temperatures.

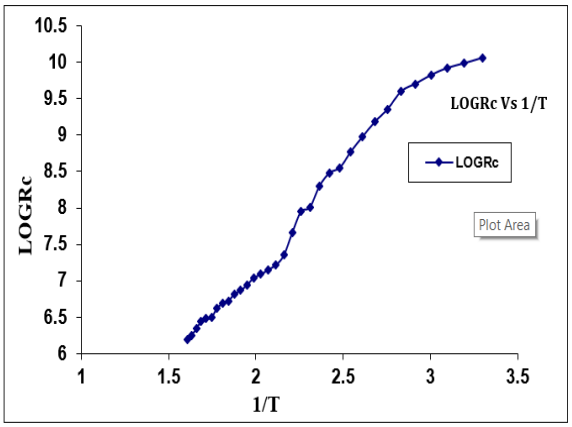

Fig.12: Plot of log R Vs 1/T for unannealed NiO thick films.

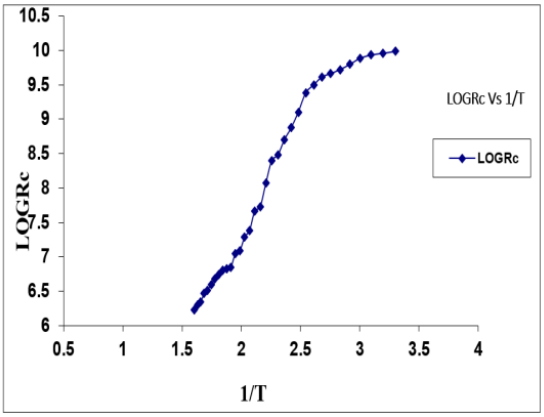

Fig. 13: Plot of log R Vs 1/T for NiO thick films annealed at 250^0C.

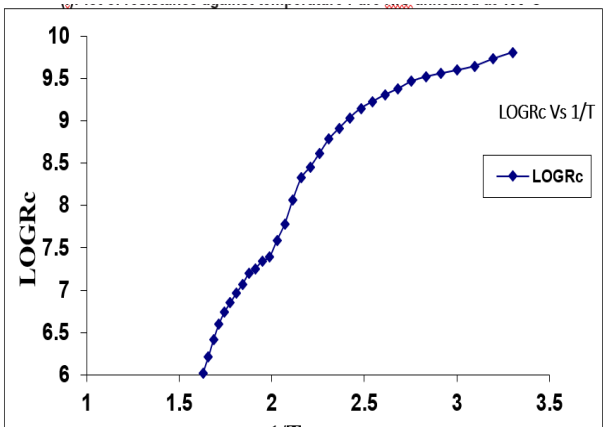

Fig. 14: Plot of log R Vs 1/T for NiO thick films annealed at 400^0C.

IV. CONCLUSIONS

NiO thick films with different thickness have been successfully deposited on glass substrates by the simple and cost-effective screen-printing technique. The structural, morphological and electrical properties have been systematically investigated for NiO thick films. The films annealed in the temperature range 250 ^{0}C to 400 ^{0}C unannealed. XRD analysis reveals that the NiO thin film shows a polycrystalline nature. Increase in the thickness of the NiO films increased the crystallinity as well as morphological properties. The average crystallite size calculated using the Debye's Scherrer equation for most intense reflection (200) at 2θ = 43.43° is 8.532 nm. From SEM, observed that particles are highly agglomerated and they are essentially cluster of nano particles. The average particle size is 175.8 nm. The grain size increases and Surface area decreases with increase in annealing temperature. Highly porous film shows high sensitivity. EDAX gives quantitative elemental analysis of Ni and oxygen and non-stoichiometric in nature. From electrical characterization, resistivity decreases with annealing temperature it means NiO thick films shows semiconductor behaviour.

ACKNOWLEDGEMENT

The authors are very much thankful to management authorities of M. G. Vidyamandir, Nashik and department of Physics, M.S.G. Arts, Science and Commerce College, Malegaon Camp, Malegaon 423203, Dist. Nashik and also the authors are gratefully acknowledged to department of Physics, SPPU Pune for providing facilities for XRD and SEM analysis.

REFERENCES

1. M.A. Abbasi, Z.H. Ibupoto, A. Khan, O. Nur, M. Willander, Mater. Lett. 108 (2013)152.
2. 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.
3. J. Kim, J. H. Yun, Y.C. Park, W. A. Anderson, Mater. Lett. 75 (2012) 99.
4. M. J. Park, J.Y. Jung, S. M. Shin, J. W. Song, Y. H. Nam, D. H. Kim, Thin Solid Films 599 (2016) 54.
5. K. C. Wang, P.S. Shen, M.H. Li, S. Chen, M.W. Lin, P. Chen, ACS Appl. Mater. Interfaces 6(15), (2014)11581.
6. J.H. Yun, J. Kim, Y.C. Park, S.J. Moon, W.A. Anderson, Thin Solid Films 547, (2013) 17.
7. S. Ahn, A.H. Tuan, S. Kim, C. Park, C. Shin, Y.J. Lee, Mater. Lett. 132, (2014) 06.
8. D. Zaouk, Y. Zaatar, R. Asmar, Microelectron. J. 37, (2006) 5.
9. A.A. Al-Ghamdi, W.E. Mahmoud, .J. Yaghmour, F.M. AlMarzouki, J. Alloy. Compd. 486, (2009) 1
10. M. Ghougali, O. Belahssen, A. Chalal Thin Film Vol. 8 No 4(2), (2016) 040591-4
11. H.-L. Chen, Y.-M. Lu, and W.-S. Hwang, Surface and Coatings Technology, 198 (2005)138.
12. Patil et. al., Bull Mater Sci, 34(1) (2011) 1.
13. Hazaa S Q, et. al. Int Journal of Latest Res in Eng. and Tech, 02 (08)(2016) 1.
14. Mirzaei A et. al., Kor Journal of Physical Society, 69 (3)(2016)373.
15. U. J. Tupe, M.S. Zambare, A.V. Patil and P. B. Koli, Material Science Research India 17(3)(2020)260.
16. B. Ramasubba Reddy, G. S. Harish, Ch. Seshendra Reddy, P. Sreedhar a Reddy Int. J. of Modern Eng. Res 4 (2014) 62.
17. B. D. Cullity, Elements of X-ray diffraction (Addison -Wesley) (1970) P102.
18. U. P. Shinde, R. S. Gosavi Int. J of Innov. Tech. and Explo. Engg. 9(7) (2020) 894.

Published By:
Blue Eyes Intelligence Engineering
and Sciences Publication

AUTHORS PROFILE

Prof. Ujwala M. Pagar, currently working as Assistant Professor in Physics at H.P.T. Arts and R.Y.K. Science College, Nashik 422005, (M.S.) India. She has 14 years of teaching experience. Published 02 Research paper in International Journal with high impact factor. Presented 2 papers in an International conference and attended several National and State level conferences.

Dr. Ugalal P. Shinde, M.Sc. Ph.D**.** Professor, Research Guide and Head Department of Electronic Science at L.V.H. Arts, Science and Commerce College, Panchavati, Nashik- 422003 (M.S) He has 33 years of teaching experience. Published 29 Research papers in various Journals. Presented 9 papers in an International conference and attended several National and State level conferences.