Optimization and characterization of NiO thin films prepared via NSP technique and its P-N junction diode application

JOSEPH SAJU^{1,*}, O.N. BALASUNDARAM²

¹Research and Development Center, Bharathiar University, Coimbatore-641046, Tamilnadu, India

²Department of Physics, PSG College of Arts and Science, Coimbatore-641014, Tamilnadu, India

The present work reports on the optimization of substrate temperature, molar concentration and volume of the solution of nickel oxide (NiO) thin films prepared by nebulizer spray pyrolysis (NSP) technique. NiO films were optimized and characterized by XRD, SEM, EDX, UV-Vis and I-V measurements. Based on XRD analysis, the molar concentration, volume of solution and substrate temperature of the prepared NiO films were optimized as 0.20 M, 5 mL and 450 °C for P-N diode applications. The XRD pattern of the optimized NiO film revealed cubic structure. The surface morphological variations and elemental composition were confirmed by SEM and EDX analysis. The optical properties were studied with UV-Vis spectrophotometer and the minimum band gap value was 3.67 eV for 450 °C substrate temperature. Using J-V characteristics, the diode parameters: ideality factor n and barrier height Φ_b values of p-NiO/N-Si diode prepared at optimum conditions, i.e. 450 °C, 0.2 M, 5 mL, were evaluated in dark and under illumination.

Keywords: *thin films; X-ray diffraction; optical and electrical properties*

1. Introduction

Transparent metal oxide (TMO) films are used in active and passive form in many applications, since they are electrically conductive and optically transparent. Among numerous TMO materials, nickel oxide (NiO) is physically stable and chemically inert, as a transparent conductor. Hence, there is an increased demand for the development of NiO thin films for optical and electronic applications. NiO is a very interesting material for different applications in both microelectronic and optoelectronic devices. It is a wide band gap oxide semiconductor with a direct energy gap of about 3.6 eV. It is a silver-white metal that is used in the preparation of electrode materials [1, 2], rechargeable batteries, catalysts, sensors [3], electrochemical capacitors and magneto-electronic devices [4].

NiO is mostly developed and used in the form of thin films; it is generally characterized in terms of thin film properties, which are somewhat different from those of the bulk material. In addition, the properties of NiO thin films are highly

dependent on the preparation conditions and parameters. Thus, several methods have been used to deposit these films, including reactive evaporation, magnetron sputtering, pulsed laser deposition, electron beam evaporation, chemical vapor deposition and chemical spray pyrolysis. Amongst these, spray pyrolysis is widely employed because of its cost effectiveness, large area productivity and easy doping. Spray pyrolysis with novel routes has been explored in this regard.

In this publication, investigations relating to the NSP technique [5–7] have been carried out. The preparation of NiO thin films on glass substrates and their structural, electrical and optical characterization have been summarized. In NSP technique, the process parameters highly govern the film properties. Hence, their optimization has been done to get high quality NiO films.

2. Experimental

2.1. NiO thin films preparation

NiO films were prepared at a substrate temperature of 450 °C with different nickel acetate concentrations of 0.05 M, 0.10 M, 0.15 M

*E-mail: sajuismyname@gmail.com

and 0.20 M. The volume of the precursor was varied as 3 mL, 4 mL, 5 mL and 6 mL for preparing the NiO films. The preliminary results gave information for fixing the concentration at 0.20 M and a low volume of 5 mL nickel precursor for all the prepared NiO films in the employed NSP pyrolysis technique. Substrate temperature was the main parameter varied in this work. The solution was prepared from 0.20 M of nickel acetate in 100 mL of triple distilled water. For increasing the solubility of the solute few drops of concentrated hydrochloric acid was added to the solution. The mixed solutions were stirred well and heated for three hours at 60 °C. Then the solution (5 mL) was sprayed onto glass substrates heated at temperatures 350 °C, 400 °C, 450 °C and 500 °C in air.

2.2. Characterization techniques

The optical properties of NiO films were examined using a UV-Vis PerkinElmer Lambda 35 spectrophotometer in the wavelength range of 300 nm to 1400 nm. An X-ray X'PERT PRO diffractometer (XRD) with CuK α 1 radiation of a wavelength 1.5406 Å at the generator settings of 30 mA and 40 kV in the 2 θ range from 20° to 70° was used to study the crystal structure. The surface morphology of the prepared films was examined under a JEOL JEM 2100 scanning electron microscope. From the energy dispersive analysis by X-ray spectroscopy (EDX) with the use of QUANTA FEG 250 SEM, the presence of elements was investigated. DC electrical properties of NiO films and the parameters of the n-NiO/p-Si junction diodes were measured by a Keithley electrometer 6517-B.

3. Results and discussion

3.1. Structural properties of NiO films

3.1.1. XRD results for NiO films deposited with different volume of spray

XRD spectra were recorded for the deposition temperature fixed at 450 °C and different volumes of nickel acetate precursor solution i.e. 3 mL, 4 mL, 5 mL and 6 mL. The XRD spectra shown in Fig. 1 include a peak at (2 2 2) corresponding to the formation of hexagonal cubic structure

(JCPDS Card No. 89-5881). The well-defined peak and minimum noise is observed for the solution volume of 5 mL, which is the optimum solution volume.

Fig. 1. XRD patterns of NiO thin films for different volumes of solution.

3.1.2. XRD results for NiO films deposited with different concentrations

XRD spectra were recorded for the deposition temperature fixed at 450 °C and different concentrations of nickel acetate precursor solution i.e. 0.05 M, 0.10 M, 0.15 M and 0.20 M. Fig. 2 shows the XRD patterns of the films deposited at different solution concentrations of nickel acetate. From the figure it is seen that the films are polycrystalline with cubic structure (JCPDS Card No. 89-5881). X-ray diffractograms show that the films have grown along (2 2 2) and (4 0 0) planes. It is further seen that 0.20 M solution concentration results in crystallinity of the film higher than for the other solution concentrations. The peaks at (2 2 2) and (4 0 0) correspond to the formation of cubic structure. The well-defined peaks are observed

for the molar concentration of 0.20 M, which is the optimum molar concentration.

Fig. 2. XRD patterns of NiO thin films for different molar concentrations.

3.1.3. Structural properties of NiO films prepared at different temperatures

The structure of the NiO thin films prepared by the NSP technique was characterized by XRD analysis. The films showed polycrystalline nature for all the deposition conditions and had lattice parameters corresponding to those of cubic NiO crystal. Properties of NiO films deposited at different temperature conditions are presented in this section. Substrate temperature is a crucial deposition parameter in NSP deposition of transparent metal oxide films. In order to study the influence of substrate temperature on the composition and crystalline properties of NiO films, substrate temperature was varied between 350 °C and 500 °C.

Structural development of NiO thin films as a function of deposition temperature is shown in Fig. 3. All the NiO films prepared at different substrate temperatures have a polycrystalline nature. XRD spectra exhibit diffraction patterns with

the peaks corresponding to cubic structure of NiO and are indexed according to the Joint Committee of Powder Diffraction Standards (JCPDS Card No. 89-5881). Investigated NiO films for the 2θ scans between 20° and 70° indicate a slightly (2 2 2) preferred orientation. For the films deposited between 300 °C and 450 °C, the increase in temperature led to an improvement in crystallinity owing to the shrinking of particles and increased packing density. The film prepared at 450 °C exhibits highly intense peaks at (2 2 2), (4 0 0), and (4 4 0) planes, respectively. The presence of the diffraction peaks indicates that the films are polycrystalline in nature. The intensity of the (2 2 2) peak and its narrowing as the substrate temperature is increased up to 450 °C (Fig. 3) indicates an improvement in the degree of crystallinity of the films, and it can be assumed that the higher substrate temperature enables the atoms to move to the stable sites [8].

Fig. 3. The XRD pattern of NiO thin films deposited at different substrate temperatures.

The crystallite size [39], microstrain ϵ and dislocation density δ values can be obtained using the following equations [9–13]:

$$D = \frac{k\lambda}{\beta \cos \theta} \quad (1)$$

$$\varepsilon = \frac{\beta \cos \theta}{4} \quad (2)$$

$$\delta = \frac{1}{D^2} \frac{\text{lines}}{m^2} \quad (3)$$

At high deposition temperature of 500 °C, the peak intensity decreases and this may be due to the evaporation of nickel salt that leads to homogeneous nucleation. From Table 1, it is evident that crystallite size of the NiO films increases with the increase in substrate temperature for the (2 2 2) oriented crystallites up to 450 °C and then decreases.

The crystal defect parameters such as microstrain and dislocation density were estimated and their variations with respect to the substrate temperature can be seen in Table 1. The microstrain shows a decreasing trend with increasing substrate temperature up to 450 °C and then increases. This type of change in strain may be due to the recrystallization process observed in the polycrystalline oxide films. At substrate temperature of 450 °C, dislocation density is maximum as shown in Table 1, which reveals the reduction in the concentration of lattice imperfections leading to highly crystallized films with preferred orientations.

3.2. Surface morphology of NiO films

The surface morphology of NiO films deposited at 350 °C, 400 °C, 450 °C and 500 °C is shown in Fig. 4. Non-uniform surface structure is observed for all the NiO films deposited at different substrate temperatures. However, the grain growth and benzene shaped nanostructure of the surface obtained at the substrate temperature of 450 °C resulted in some improvement of the surface morphology, as shown in Fig. 4c. The nanostructures were found to grow with increased substrate temperature. Randomly oriented surface morphology with larger grains is observed on the surface of NiO film deposited at 450 °C. From the morphological results, it can be inferred that NiO film can be prepared by keeping the substrate temperature at 450 °C, which is suitable for the currently studied NSP technique. The stoichiometry analysis of the elements present in the NiO thin film

was carried out from EDAX results. Fig. 4e shows the EDAX pattern of the NiO film deposited under the optimized conditions at substrate temperature of 450 °C. The atomic percentage ratio of the film prepared at temperature of 450 °C indicates the ratio of Ni:O as 33.11:27.86. From this result, the presence of Ni and O elements in the NiO thin film was confirmed.

3.3. Optical properties of NiO films

NiO films prepared by NSP technique at various substrate temperatures between 300 °C and 500 °C under the optimized deposition conditions were studied for their optical properties. The optical absorbance curves of NiO films have been obtained in the 300 nm to 1400 nm spectral region.

Fig. 5 depicts the optical absorbance spectra of the NiO films deposited under optimized conditions at different substrate temperatures. The value of absorbance in the UV-Vis region is found to increase with increasing deposition temperature. The maximum absorbance value is observed for the NiO films prepared at 450 °C. The increase in absorbance is attributed to the well adherent films and their nanocrystalline nature as revealed by the XRD results, which explicitly shows high peak intensities due to uniform oxidation of NiO film and improvement in the lattice atomic arrangement. In case of higher substrate temperatures above 450 °C, there is a drop in absorbance due to the increased surface irregularity and impaired crystallinity. Evaporation of mist like solute in the NSP process at high deposition temperature led to the films with lower stoichiometry. The crystallinity deviation produced less intense peak as evidenced from the XRD results for the NiO films deposited at higher temperatures.

From the UV-Vis result, the optical band gap of the nanocrystalline NiO films was evaluated. The optical absorption α related to the optical band gap of the prepared films at different substrate temperatures satisfies the relation $\alpha h\nu = A (h\nu - E_g)^{1/2}$ [14, 15]. A typical plot is presented in Fig. 6. It can be observed that the plot is linear in the region of strong

Table 1. The microstructural properties of NiO thin films for different substrate temperatures.

Substrate temperature [°C]	(2 2 2) diffraction angle 2θ [°]	Crystallite size (D) [nm]	Microstrain (ε) [10 ⁻³ lines ⁻² .m ⁻⁴]	Dislocation density [10 ¹⁴ lines/m ²]
350	37.1176	11.65	2.9676	1.165
400	37.2417	17.06	2.0333	3.436
450	37.2639	34.12	1.0166	8.589
500	37.1839	19.98	1.7360	2.505

Fig. 4. (a-d) SEM images of NiO thin films deposited at different substrate temperatures of 350 °C, 400 °C, 450 °C and 500 °C and (c) EDX spectrum of NiO thin film obtained at 450 °C.

absorption, i.e. near the fundamental absorption edge seen at the ultraviolet region. The linear intercept at the $h\nu$ axis gives the direct allowed band gap values of 3.77 eV, 3.75 eV, 3.67 eV and 3.70 eV. The minimum band gap value is obtained for the NiO film prepared at 450 °C. The estimated values for NiO are in good agreement with the previously reported values [16, 17].

3.4. DC electrical properties

I-V measurements of NiO thin films prepared with various volumes of solution, mole concentrations and substrate temperatures were taken at room temperature through two probe method using a Keithley electrometer. The current values were measured for different applied voltages from

10 V to 100 V (Fig. 7a, Fig. 8a and Fig. 9a). The DC conductivity σ for NiO films was calculated using the equation 4 [6, 7, 18]:

$$\sigma = \left(\frac{I}{V} \right) \times \left(\frac{d}{A} \right) \quad (4)$$

where I is the current, V is applied potential, d is inter-probe distance and A is cross-sectional area of the film.

Fig. 7a shows the I-V characteristics of NiO films for different volume concentrations. The obtained average conductivity values are 2.067×10^{-10} S/cm, 2.578×10^{-10} S/cm, 2.877×10^{-10} S/cm and 2.711×10^{-10} S/cm for solution volume from 3 mL to 6 mL. The results reveal that the conductivity value increases

Fig. 5. UV-Vis analysis of NiO thin films deposited at different substrate temperatures.

Fig. 6. The band gap energy of NiO thin films deposited at different substrate temperatures.

up to 5 mL and then decreases as shown in Fig. 7b. Fig. 8a shows the I-V characteristics for different molar concentrations. The average conductivity values of NiO films obtained are 1.459×10^{-11} S/cm, 1.630×10^{-11} S/cm, 1.783×10^{-11} S/cm and 2.091×10^{-11} S/cm for different molar concentrations of 0.10 M, 0.15 M, 0.20 M and 0.25 M. From Fig. 8b, the maximum conductivity is observed for 0.20 M concentration.

The I-V characteristics for different substrate temperatures are shown in Fig. 9a.

Fig. 7. (a) I-V characterization of NiO thin films and (b) average conductivity values for different volumes of solution.

By varying the substrate temperature from 350 °C to 500 °C, the observed average conductivity values of NiO films have changed as 1.175×10^{-11} S/cm, 2.498×10^{-11} S/cm, 3.343×10^{-11} S/cm and 2.907×10^{-11} S/cm. At the substrate temperature of 450 °C, the maximum conductivity value is found as shown in Fig. 9b. The variations in conductivity values may be attributed to the oxygen vacancies in the prepared NiO thin films [7, 19–21]. The increase in conductivity with the substrate temperature resulted from the variation in morphology and the increase in grain size up to 450 °C, which reduced the lattice dislocations and imperfections of the Ni–O matrix. This phenomenon decreases the grain boundary volume associated with the flow of charge carriers [22].

Fig. 8. (a) I-V characterization of NiO thin films and (b) average conductivity values for different molar concentrations.

Fig. 9. (a) I-V characterization of NiO thin films and (b) average conductivity values for different substrate temperatures.

3.5. I-V characterization of p-NiO/n-Si junction diode

The P-N junction diode of p-NiO/n-Si was prepared by NSP technique based on the optimized results i.e. volume of solution 5 mL, molar concentration 0.20 M and substrate temperature 450 °C. The prepared p-NiO/n-Si junction diode parameters with ideality factor n and barrier height Φ_b were measured under dark and illumination conditions. The reverse to forward bias current measurement was taken for the applied potential of -4 V to $+4$ V. Fig. 10 shows the I-V characteristics of p-NiO/n-Si junction diode under dark and illumination. Fig. 11 illustrates the semi-log plot of the current density $\ln J$ vs. voltage V . From Fig. 10 it is seen that the p-NiO/n-Si junction diode

exhibits good rectifying nature in dark and under illumination.

Using the thermionic emission (TE) equations, the current density of the p-NiO/n-Si junction diode was calculated as follows [23, 24]:

$$J = J_0 \exp \left(\frac{qV}{nKT} - 1 \right) \quad (5)$$

where J_0 is density of reverse saturation current, q is the charge of electron, V is the applied potential, n is the ideality factor, K is the Boltzmann constant and T is absolute temperature.

Using equation 5 for $V \geq 3kT/q$, n and J_0 values were obtained from the slope and interception of semi-log forward bias J-V plot.

Thus, n and Φ_b were calculated by the following equations [23, 24]:

$$n = \frac{q}{KT} \frac{dV}{d(\ln J)} \quad (6)$$

$$\Phi_b = \frac{KT}{q} \ln \left(\frac{AA^*T^2}{J_0} \right) \quad (7)$$

where A is the active area of prepared diode and A^* is the Richardson constant. The n and Φ_b values under darkness were obtained as 4.9 and 0.79 eV and under light illumination as 4.1 and 0.80 eV, respectively. The n value is unity (i.e. $n = 1$) for an ideal P-N diode but in the present work, the n values higher than unity were obtained. The results suggest the non-ideal behavior of prepared p-NiO/n-Si junction diode which may be caused by the presence of native oxide layer (SiO_2) and barrier inhomogeneity [25, 26].

Fig. 10. I-V characteristics of NiO thin film deposited at the substrate temperature of 450 °C in darkness and under light.

4. Conclusions

Nickel oxide films have been prepared successfully using NSP technique. The influences of the spray parameters like volume, molar concentration of the precursor solution and temperature of the substrate on the film growth, its structural, and electrical properties have been studied.

Fig. 11. $\ln J$ vs. voltage plots of NiO thin film deposited at the substrate temperature of 450 °C in darkness and under light.

0.20 M of nickel acetate, 5 mL volume of the solution and the deposition temperature of 450 °C were the optimized deposition parameters to prepare NiO films in the present study. The XRD result showed the cubic structure of the NiO films. The SEM result revealed randomly oriented surfaces of the films. The optical properties of the NiO films, (optical band gap) were estimated from UV-Vis spectra. The maximum absorbance and the minimum band gap value of 3.67 eV were observed for the film deposited at 450 °C. Using electrical analysis, 0.20 M of nickel acetate, 5 mL volume of the solution and substrate temperature of 450 °C were assumed as optimal parameters for the deposition process. From I-V characteristics, p-NiO/n-Si junction diode parameters were calculated as $n = 4.9$ in dark and $n = 4.1$ under light. This photoresponse behavior makes these diodes suitable for photodetector applications.

References

- [1] NARDI J.C.Z., *J. Electrochem. Soc.*, 132 (1985), 1787.
- [2] SANCHEZ L., FARAY J., PEREIRA RAMOS J.P., HERMAN L., MORALES J., TIRADO L., *J. Mater. Chem.*, 6 (1996), 37.
- [3] XU C.N., MIYAZAKI K., WATANABE T., *Sensor. Actuat. B-Chem.*, (1998), 46.
- [4] PATIL, P.S. KADAM. L.D., *Appl. Surf. Sci.*, 199 (2002), 211.

- [5] SETHUPATHI N., THIRUNAVUKKARASU P., VIDHYA V.S., THANGAMUTHU R., KIRUTHIKA G.V.M., PERUMAL K., BAJAJ H.C., JAYACHANDRAN M., *J. Mater. Sci.-Mater. El.*, 23 (2012), 1087.
- [6] BALAJI M., CHANDRASEKARAN J., RAJA M., *Mater. Sci. Semicond. Proc.*, 43 (2016), 104.
- [7] BALAJI M., CHANDRASEKARAN J., RAJA M., RAJESH S., *J. Mater.-Sci. Mater. El.*, 27 (2016), 11646.
- [8] CHAABOUNI F., ABAAB M., REZIG B., *Mater. Sci. Eng. B-Adv.*, 109 (2004), 236.
- [9] SCHERRER P., *Nachr. Ges. Wiss. Gottingen*, 1918 (1918), 98.
- [10] SURESH R., PONNUSWAMY V., MARIAPPAN R., SENTHIL KUMAR N., *Ceram. Int.*, 40 (2014), 437.
- [11] MARIAPPAN R., PONNUSWAMY V., SURESH P., *Superlattice. Microst.*, 52 (2012), 500.
- [12] RAJA M., CHANDRASEKARAN J., BALAJI M., *Silicon*, 9 (2017), 201.
- [13] MAHALINGAM T., THANIKAIKARASAN S., DHANASEKARAN V., MARIAPPAN R., JAYAMURUGAN P., VELUMANI S., JIN-KOO RHEE, *Mater. Sci. Eng. B-Adv.*, 174 (2010), 249.
- [14] TAUC J., *Mater. Res. Bull.*, 3 (1968), 37.
- [15] RAUT B.T., PAWAR S.G., CHOUGULE M.A., SHASHWATI SEN, PATIL V.B., *J. Alloy Compd.*, 509 (2011), 9065.
- [16] Jlassi M., Sta I., Hajji M., Ezzaouia H., *Appl. Surf. Sci.*, 308 (2014), 199.
- [17] NALAGE S.R., CHOUGULE M.A., SHASHWATI SEN, JOSHI P.B., PATIL V.B., *Thin Solid Films*, 520 (2012), 4835.
- [18] MANICKAM M., PONNUSWAMY V., SANKAR C., MARIAPPAN R., SURESH R., *Silicon*, 8 (2016), 351.
- [19] NIRUPAMA V., CHANDRASEKHAR M., RADHIKA P., SREEDHAR B., UTHANNA S., *J. Optoelectron. Adv. M.*, 11 (2009), 320.
- [20] NIRUPAMA V., CHANDRA SEKHAR M., SUBRAMANYAM T.K., UTHANNA S., *J. Phys. Conf. Ser.*, 208 (2010), 012101.
- [21] SUTRAVE D.S., GOTHE S.D., *DAMA Int.*, 2 (2015), 1.
- [22] RAJA M., CHANDRASEKARAN J., BALAJI M., JANARTHANAN B., *Mater. Sci. Semicond. Proc.*, 56 (2016), 145.
- [23] GUPTA R.K., GHOSH K., KAHOL P.K., *Physica E*, 42 (2010), 1509.
- [24] MAYIMELE M.A., DIALEN M., MTANGI W., AURET F.D., *Mater. Sci. Semicond. Proc.*, 34 (2015), 359.
- [25] RHODERICK E.H., WILLIAMS R.H., *Metal-semiconductor Contacts*, 2nd Ed., Clarendon Press, Oxford, 1988.
- [26] WANG C.X., YANG G.W., LIU H.W., HAN Y.H., LUO J.F., GAO C.X., ZOU G.T., *Appl. Phys. Lett.*, 84 (2004), 2427.

Received 2017-06-05

Accepted 2018-12-03