J. Nano- Electron. Phys.
3 (2011) No1, P. 376-382

PACS numbers: 72.80.Ga, 81.15.Ef, 61.05.C – , 78.20. – e, 73.40.Lq

p-TYPE TRANSPARENT NiO THIN FILMS BY e-BEAM EVAPORATION TECHNIQUES

***K.J. Patel*[1], *M.S. Desai*[1], *C.J. Panchal*[1], *Bharati Rehani*[2]**

[1] Applied Physics Department, Faculty of Technology & Engineering,
The M. S. University of Baroda, Vadodara 390001, Gujarat, India
E-mail: cjpanchal_msu@yahoo.com

[2] Metallurgical and Materials Engineering Department,
Faculty of Technology & Engineering
The M. S. University of Baroda, Vadodara 390001, Gujarat, India

Nickel oxide (NiO) semiconductors thin films were prepared by e-beam evaporation technique at different substrate temperatures ranging from room temperature to 400 °C *on glass substrate. Glancing incident X-ray diffraction depict that with the increases in substrate temperature the preferred orientation changes from* (111) *to* (200) *direction. Atomic force microscopy was used to investigate the surface morphology of the NiO thin films. The transmittance of NiO thin film increases with substrate temperature. NiO thin film was also deposited on n-type indium tin oxide (ITO) thin films to investigate the diode characteristic of p-NiO/n-ITO junction.*

Keywords: *VACUUM DEPOSITION, GLANCING INCIDENT X-RAY DIFFRACTION (GIXRD), NiO THIN FILM, p-TYPE SEMI-CONDUCTOR, p-n JUNCTION.*

(Received 04 February 2011, in final form 27 April 2011)

1. INTRODUCTION

Transparent conducting oxides (TCO) having a combination of electrical conductivity and optical transparency is used in many technological applications viz. photovoltaic, flat panel display, electrochromic device [1, 2]. Today indium tin oxide (ITO), fluorine-doped tin oxide (FTO), aluminum-doped zinc oxides (AZO) is in practical use for TCO [3, 4]. All these TCOs show the n-type behaviors due to oxygen vacancies and anion interstitials which create the free electrons. The p-type semiconductor TCO is important for the fabrication of transparent conducting p-n junction for many optoelectronic devices [5, 6]. It has been found that nickel oxide (NiO) is nearly transparent, wide band-gap semiconductor and it shows p-type semi-conducting behavior. A “slightly” non-stoichiometric composition in NiO thin film occurs due to acquisition of an excess of oxygen (which is compensated by the oxidation of some Ni^{2+} to Ni^{3+}) and is responsible for the p-type semi-conducting behaviors. The conductivity of NiO thin films has dependence on the formation of micro-structural defects, such as nickel vacancies and interstitial oxygen in NiO [7]. In literature most of NiO thin films were grown by sputtering, pulse laser deposition, and chemical bath deposition methods [8-10]. In the present study the NiO thin films were grown by e-beam evaporation technique on glass substrate held at room temperature (RT) to 400 °C. The effect of substrate temperature on structural, surface morphology, and optical properties was investigated. A p-NiO/n-ITO junction has been fabricated to confirm the p-type semi-conducting behavior of nickel oxide thin film for its potential device applications.

2. EXPERIMENTAL

NiO thin films were deposited on organically cleaned soda-lime glass substrate by e-beam evaporation. NiO powder (Sigma Aldrich, 99.9 %) was used as source material. The substrate temperature was varied from RT to 400 °C using radiant substrate heater and monitored using Cr-Al thermocouple. The thickness of the film 2500 Å at the rate of deposition 4 Å/s was monitored and controlled by quartz crystal based thin film deposition controller (Sigma Instruments, SQC 122c). For the formation of p-n junction the NiO thin films were deposited on ITO coated glass substrate having a sheet resistance of ~ 5 Ω/□. The crystallographic structure of NiO thin films were characterized by glancing incident X-ray diffraction (GIXRD) with a Bruker D8 diffractometer using an CuK_α radiation (λ = 1.542 Å) at an incident angle 0.5°. The surface morphology of the thin film was investigated by atomic force microscopy (AFM). The optical measurement was performed using dual beam UV-Visible spectrophotometer (Shimadzu UV-2450) in the wavelength range of 300-900 nm. The sheet resistance of the NiO thin films was measured using the standard four-probe method and the current-voltage (I-V) characteristic of p-NiO/n-ITO junction were measured using Keithley 2420C source meter.

3. RESULTS AND DISCUSSIONS

3.1 Structural and morphological properties

The XRD spectra of NiO thin films deposited on glass substrates held at different temperatures are shown in Fig. 1.

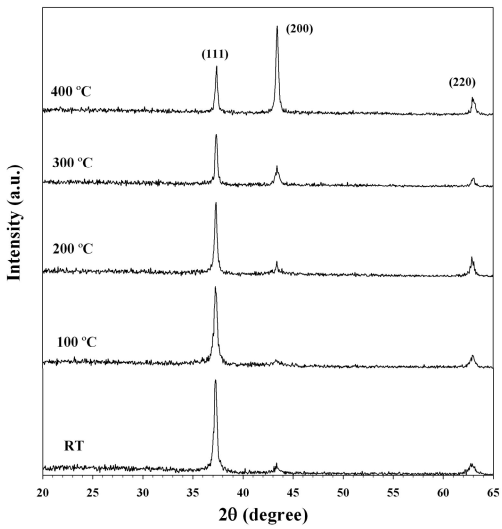

Fig. 1 *– XRD spectra of NiO thin films at different substrate temperatures*

From the Fig. 1 the film deposited from RT to 400 °C are polycrystalline in nature with a cubic structure. The films deposited at RT to 300 °C shows the (111) preferred orientation with (200) and (220) minor orientations. The intensity of the (111) peak decreases while the intensity of the (200) peak increases with the substrate temperature i.e. the (200) preferred orientations improve with substrate temperature. The intensity of (220) peak increases up to 200 C and then the slight decreases in intensity is observed with further increases in substrate temperatures. At 400 °C the preferred orientation changed from (111) to (200) directions. At the higher substrate temperature (~ 400 °C) in NiO thin films the non-stoichiometry decreases and thus the films orientation changes from (111) direction into (200) directions [8]. The inter-plane spacing (d-value) can be calculated using $d = \lambda/2\sin\theta$ are presented in Table 1, where λ is the X-ray wavelength and θ is the Bragg's angle. The d value slightly decreased with substrate temperature due to the change in the composition and the crystal structure of the films with substrate temperature. The crystallite size (D) was determined from the full width half maxima (FWHM) of major XRD peaks using the Scherrer's equation [11],

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

where, k is the shape factor (0.9), λ is the X-ray wavelength, and θ is the Bragg's angle. The d value of the peak, the FWHM, and the crystalline size of the NiO thin films with different substrate temperatures estimated from the XRD spectra are presented in table 1.

Table 1 – *The d-value, the FWHM, and the crystalline size of the NiO thin films in* (111), (200) *and* (220) *orientations for different substrate temperatures*

Substrate tempera-ture, °C	d-value, Å			FWHM			Crystalline size, nm		
		(200)	(220)	(111)	(200)	(220)	(111)	(200)	(220)
RT	2.4141	-	1.4791	0.4396	-	1.1489	20	-	8
100	2.4116	-	1.4773	0.5440	-	0.7707	16	-	13
200	2.4109	-	1.4775	0.4029	-	0.5967	22	-	17
300	2.4079	2.0834	1.4760	0.3287	0.7721	0.5451	27	12	18
400	2.4073	2.0838	1.4692	0.3808	0.3612	0.5440	23	25	18

The surface morphology of the NiO thin film deposited at different substrate temperature was observed by AFM. Fig. 2 shows the AFM images with the area of 1 μm × 1 μm of the NiO thin films on the glass substrates deposited at RT to 400 °C substrate temperature.

The AFM observation shows that the grain size of the films increases up to 200 °C and then it was decreases with further increases in the substrate temperature due to change in the preferred orientation and the columnar grain growth [12]. The root mean square (rms) surface roughness of the thin films was measured from the AFM images are shown in Fig. 3. The film

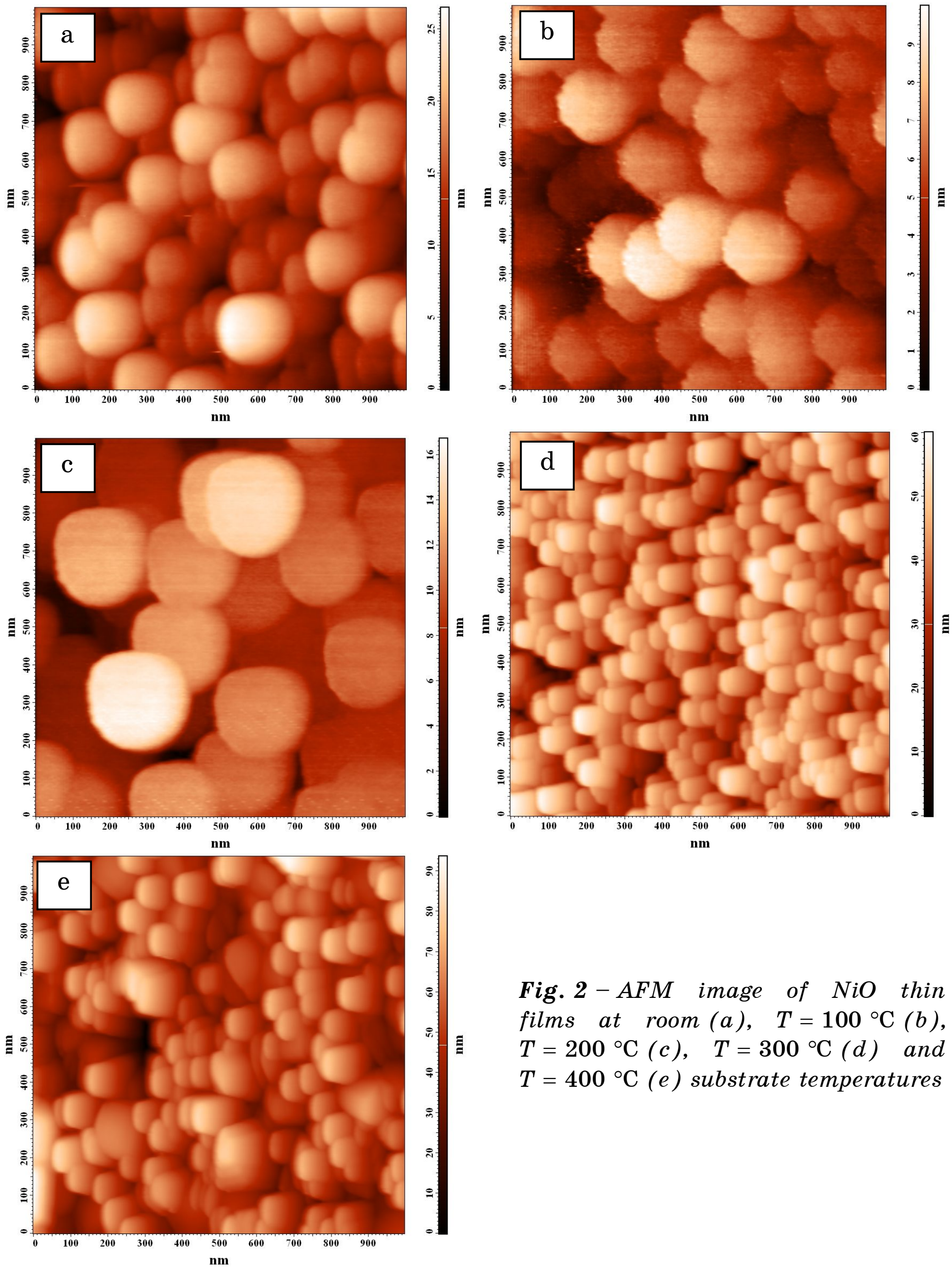

Fig. ***2*** *– AFM image of NiO thin films at room (a), T* = 100 °C *(b), T* = 200 °C *(c), T* = 300 °C *(d) and T* = 400 °C *(e) substrate temperatures*

deposited at RT to 200 °C shows the slight less surface roughness compare to other higher substrate temperature deposition films further increases in the substrate temperature due to the columnar grin growth the surface roughness increases.

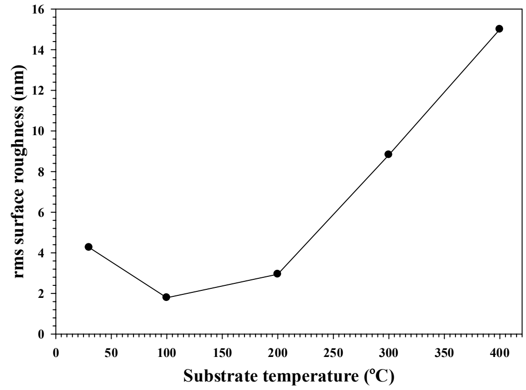

Fig. 3 *– The rms surface roughness of the NiO thin films deposited different substrate temperatures*

3.2 Optical properties

The optical transmittance spectra of NiO thin films deposited on glass substrates at different substrate temperatures are presented in Fig. 4 a. It can be seen that the film prepared at unheated substrate exhibit gray in color with ~ 50 % transmittance. As the increase in the substrate temperature of the films causes an increase in the transmittance. The lower transmittance is associated with an excess of oxygen in the lattice which creates Ni^{3+} ions and this produced as color centers. The transmittance increases with substrate temperature is due to the less defect-scattering (Ni^{3+}) and improvement of crystalline microstructure of the films.

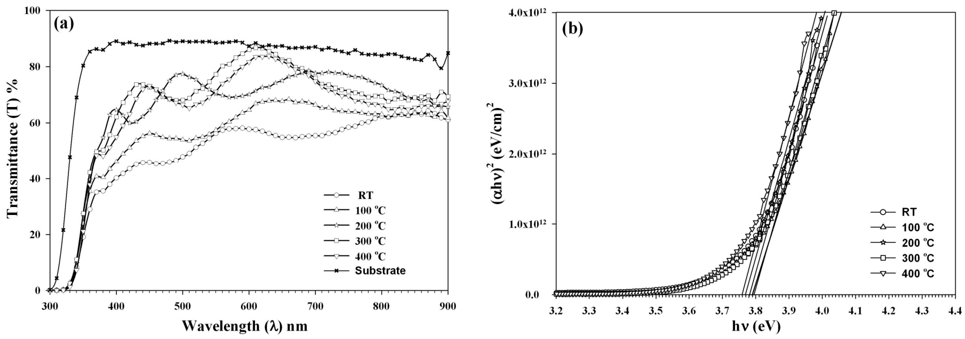

Fig. 4 *– Transmittance spectra (a) and $(\alpha h\nu)^2$ vs. $(h\nu)$ plot (b) for NiO thin films obtained at different substrate temperatures*

A strong absorption in the UV region is observed at wavelength ~ 325 nm which is attributes to the fundamental band edge of NiO. The optical absorption coefficient α of the NiO thin films as a function of transmittance was given by $\alpha = 1/d{\cdot}\ln(1/T)$. The optical energy band gap E_g of the NiO thin films can be determined from the dependence of absorption coefficient on the photon energy using the relation $\alpha h\nu = B{\cdot}(h\nu - E_g)^n$ [13], where n depends on the nature of transition in the materials. NiO shows the allowed direct transition so the energy band gap E_g could be obtain by ploting $(\alpha h\nu)^2$ vs. $(h\nu)$ plot and extrapolating the linear portion to $(\alpha h\nu)^2 = 0$ as shown in Fig. 4 b. The value of E_g varies in the range 3.76 to 3.79 eV as the substrate temperature increases from RT to 400 °C. The change in the optical band gap is due to the change in stoichiometry and crystallinity in the film.

3.3 Electrical properties

The type of conductivity of NiO thin film deposited at RT to 400 °C substrate temperature was examined by the hot-probe method, which exhibit p-type semi-conducting behaviors. The electrical properties of NiO thin films deposited at low substrate temperature (RT to 300 °C) are unstable in the atmosphere. From the XRD results the films grown at RT to 300 °C substrate temperature shows the (111) preferred orientation which is unstable due to dangling bonds while the films deposited at 400 °C show the (200) preferred orientation which is stable compared to the (111) orientation. Thus the electrical aging rate significantly drops at high substrate temperature [14]. The electrical resistance of the NiO thin films grown at 400 °C substrate temperature was measured using the four-probe method is 470 MΩ/□ and the resistivity is 1.88×10^{-1} Ω·cm.

3.4 p-n junction characteristics

In order to examine the p-type semi-conducting behavior of NiO thin films, a p-n junction formed by depositing it on n-ITO coated glass substrate held at 400 °C substrate temperature. I-V characteristic and the transmittance spectra of the p-NiO/n-ITO junction are illustrated in Fig. 5.

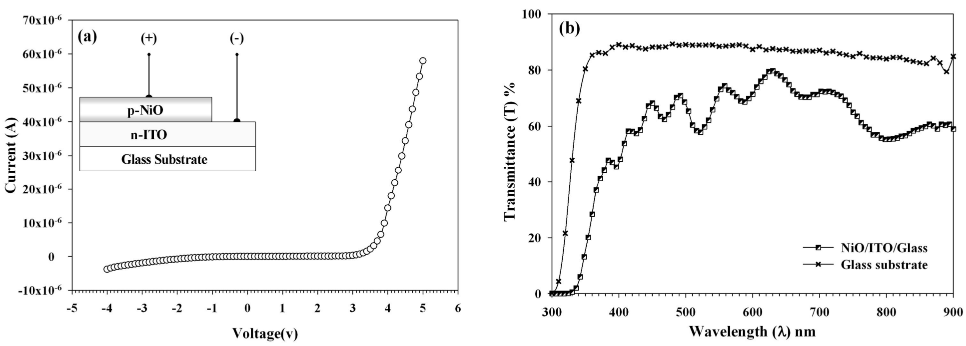

***Fig. 5** – I-V characteristics with the p-n diode structure (a) and transmittance spectra (b) of the p-NiO/n-ITO junction*

Fig. 5a shows a typical rectifying behavior of thin film p-n junction diode which exhibited a threshold voltage of 3.4 V. The inserted image shows the p-NiO/n-ITO/Glass multilayered structure. p-n junction has an average transmittance 60-65 % in the visible region of light as shown in Fig. 5b. This p-n-junction diode is suitable for many applications as a transparent p-n junction but further investigation on p-NiO/n-ITO junction based devices will be required.

4. CONCLUSION

n-NiO semi-conducting thin films were prepared by the e-beam evaporation technique. From the GIXRD measurement, the preferred orientation change from (111) to (200) direction with increasing substrate temperature. At the higher substrate temperature 300 °C and 400 °C due to the columnar grin growth the surface roughness increases. The transmittance of NiO thin film increases with substrate temperature and the band gap lies in the range 3.76 to 3.79 eV. All the thin films deposited at RT to 400 °C substrate temperatures exhibit p-type semi-conducting properties. The NiO films deposited at 400 °C have more stable phase with resistivity of 1.88×10^{-1} Ω·cm. p-NiO/n-ITO junction show the typical rectifying behaviors with the average 60-65 % transmittance in the visible region of light.

A part of this work was performed at UGC-DAE Consortium for Scientific Research, Indore, and also thankful to UGC for providing a financial assistance to the department under DRS [file no. 530/2/DRS/2007(SAP-1)]. One of the authors, Mr. K.J. Patel, is also thankful to The M.S. University of Baroda, Vadodara, for providing financial support under the university research scholarship.

REFERENCES

1. E. Fortunato, D. Ginley, H. Hasono, D.C. Paine, *MRS Bull.* **32,** 242 (2007).
2. C.G. Granqvist, A. Hultaker, *Thin Solid Films* **411,** 1 (2002).
3. T. Minami, *Semicond. Sci. Technol.* **20,** S35 (2005).
4. K.L. Chopra, S. Major, D.K. Pandya, *Thin Solid Films* **102,** 1 (1983).
5. H. Ohta, K. Kawamura, M. Orita, M. Hirano, N. Sarukura, H. Hosono, *Appl. Phys. Lett.* **77,** 475 (2000).
6. J.F. Wager, D.A. Keszler, R.E. Presley, *Transparent Electronics*, (New York, USA: Springer Science: 2008).
7. E. Antolini, *J. Mater. Sci.* **27,** 3335 (1992).
8. W.L. Jang, Y.M. Lu, W.S. Hwang, T.L. Hsiung, H.P. Wang, *Surf. Coat. Tech.* **202,** 5444 (2008).
9. I. Fasakia, A. Koutoulakia, M. Kompitsasb, C. Charitidis, *Appl. Surf. Sci.* **257,** 429 (2010).
10. M.A. Vidales-Hurtado, A. Mendoza-Galvan, *Mater. Chem. Phys.* **107,** 33 (2008).
11. B.D. Cullity, S.R. Stock, *Elements of X-ray Diffraction*, (New Jersey, USA: Prentice Hall: 2001)
12. H.-L. Chen, Y.-M. Lu, W.-S. Hwang, *Thin Solid Films* **514,** 361 (2006).
13. J. Tauc, *Amorphous and Liquid Semiconductors*, (London, Great Britain: Plenum: 1974).
14. H.L. Chen, Y.M. Lu, W.S. Hwang, *Surf. Coat. Tech.* **198,** 138 (2005).