

## Research Article

## Influence of Growth Temperature on the Properties of DC Reactive Magnetron Sputtered NiO Thin Films

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### Abstract

Nickel oxide (NiO) films were deposited on Corning 7059 glass substrates using DC reactive magnetron sputtering at different substrate temperatures in the range 30°C to 400°C. The effect of substrate temperature (Ts) on the structure, chemical binding configuration, surface morphology, composition, optical and electrical properties of NiO films was investigated. X-ray diffraction studies indicated that as Ts increased above 200°C; the preferred orientation (220) intensity was increased and had a stable cubic structure. The X-ray photoelectron spectroscopy studies revealed the grown films have single phase of NiO. From the morphological studies, it was observed that the grain size and root mean square roughness was increased with Ts. It is suggested that the growth temperature affects the properties of NiO film. Higher substrate temperature induces larger grain size and more perfect crystalline structure, which lead to low resistivity.

**Keywords:** Nickel oxide, Sputtering, Thin film, Substrate temperature, Grain size, Resistivity.

### 1. Introduction

Perfect control of oxide thin film synthesis and processing is an important role in a variety of technological applications in several fields. Nickel oxide (NiO), a p-type semiconducting oxide (in contrast to most oxides which are n-type), has been utilized as thin film sensors (Kumagai, *et al*, 1996), electronic devices (Makimura, *et al*, 2006), heterojunction solar cells (Bandara, *et al*, 2004), electrochromic display devices (Kitao, *et al*, 2004) and p-type transparent conducting films (Sato, *et al*, 1993) due to their excellent chemical stability as well as optical and electrical properties. NiO is an interesting candidate of this class with a wide band gap in the range of 3.6–4.0 eV with face centered cubic structure and have a lattice parameter of 0.4176 nm (Swagten, *et al*, 1996). Several experimental studies for preparing NiO thin films were reported by physical and chemical methods such as spray pyrolysis (Desai, *et al*, 2006), electron beam evaporation (Agrawal, *et al*, 1992), pulsed laser deposition (Tanaka, *et al*, 1996), plasma enhanced chemical vapor deposition (Yeh and Matsumura, 1997) and reactive magnetron sputtering (Mallikarjuna Reddy, *et al*, 2011). Among all these methods reactive magnetron sputtering deposition is particularly attractive due to its low cost, uniform elemental distribution and reliable capability for large area deposition (Huang, *et al*, 2011), (Wang, *et al*, 2011).

The crystallization, morphological, optical and electrical properties of NiO thin films mainly depend on the deposition parameters such as substrate temperature,

oxygen partial pressure, sputtering power, sputtering pressure, substrate bias voltage and film thickness. It is well known that the properties of as-deposited thin films will be influenced by the substrate temperature (Ts) during deposition (Wang, *et al*, 2011), (Lu, *et al*, 2007), (Abdelmoumen, *et al*, 2008). Since, the density of the point defects and dislocations in the films are modified by applying different substrate temperatures.

To the best of our knowledge, the effect of Ts on the properties of NiO thin films using magnetron sputtering is still not well studied. In this work, we deposited the NiO thin films using dc reactive magnetron sputtering at different Ts and studied the effect of Ts on the structural, surface morphological, chemical, optical and electrical properties.

### 2. Experimental

All NiO thin films were deposited on Corning 7059 glass substrates in a pure argon and oxygen (99.99%) atmosphere using 99.99% purity of Ni (100 mm diameter and 3 mm thickness) target using DC reactive magnetron sputtering technique. The chamber base pressure was approximately  $5 \times 10^{-6}$  mbar. All substrates were ultrasonically cleaned with acetone, ethanol and deionised water. In addition, the target was pre-sputtered for 10 min to remove the surface oxide layers if any on the surface of the target. The growth was performed by keeping the substrate temperatures from RT (30°C) to 400°C. The substrate temperature was monitored by means of a thermocouple placed in thermal contact with the sample

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holder. The optimized parameters during the deposition are listed in Table 1.

**Table 1** Deposition conditions of the DC magnetron sputtered NiO films

Deposition parameter	Values
Substrate temperature	30–400°C
Target to substrate distance	70 mm
Deposition time	10 min.
Sputtering power	100 W
Oxygen partial pressure	5 x 10 <sup>-4</sup> mbar
Sputtering pressure	2 x 10 <sup>-3</sup> mbar

The structural properties of the films were analysed by Seifert 3003TT X-ray diffractometer, using Cu K $\alpha$  radiation ( $\lambda=0.1546$  nm). The X-ray photoelectron spectroscopy (XPS) studies were performed to evaluate the chemical binding states using SPECS GmbH spectrometer (Phoibos 100 MCD Energy Analyzer). The surface morphology of the films was characterized by scanning electron microscopy (SEM) of model Carl Zeiss EVO ma 15 and atomic force microscopy (AFM) of model SPA 400. The chemical composition of the films was analysed by energy dispersive spectroscopy (EDS) attached with SEM of model Oxford instruments Inca Penta FET x3. In order to study optical properties of the films, the transmittance measurements were carried out by using a Perkin Elmer Lambda 950 UV-Vis-NIR spectrophotometer with a wavelength resolution better than  $\pm 0.2$  nm at room temperature. The resistivity, mobility and carrier concentration of the films were calculated by using an Ecopia Hall effect measurement system (HMS-3000VER 3.51.3).

### 3. Results and discussion

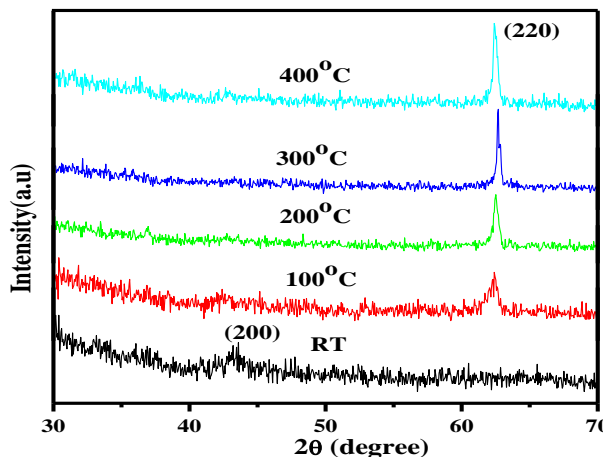
All The properties of the NiO films were highly influenced by the temperature of the substrate maintained during the growth of the films.

#### 3.1 Structural properties

##### 3.1.1 X-ray diffraction analysis

The XRD patterns of NiO films deposited at various substrate temperatures are shown in Fig. 1. The crystal structure of the films deposited at various substrate temperatures was identified to be polycrystalline and retained the cubic structure (JCPDS data No. 78-0643). From XRD spectra, we observed that the films prepared at 30°C (room temperature) exhibited (200) orientation. As the substrate temperature increased to 100°C, the preferred orientation moved to (220) plane and the (200) peak disappeared. This can be ascribed to increase in thermal energy of adsorbed atoms at higher substrate temperatures (Jang, et al, 2008). A decrease in the intensity of the (200) peak with increasing substrate temperature was previously reported (Fujji, et al, 1996). On further increasing the substrate temperature to 400°C the intensity of the (220) peak increased and becomes sharper. The crystalline phase

was build up when the depositing atoms should have sufficient energy. This gives the atoms of sufficient mobility to position them and low energy positions leading to the formation of crystalline phases. High substrate temperatures can achieve the sufficient energy to generate crystalline phases.



**Fig.1** X-ray diffraction profiles of NiO films at various substrate temperatures

The influence of growth temperature on crystallite size (L) of the films was calculated using Debye-Scherrer's equation (Cullity, 1978),

$$L = K\lambda/\beta\cos\theta \tag{1}$$

where K denotes the Scherrer's constant (K=0.94),  $\lambda$  is the wavelength of the Cu K $\alpha$  radiation ( $\lambda=0.1546$  nm),  $\beta$  full width at half maximum (FWHM) of a Gaussian fit and  $\theta$  half diffraction angle. The crystallite size and lattice parameters of the deposited films were calculated from the XRD pattern and are listed in Table 2.

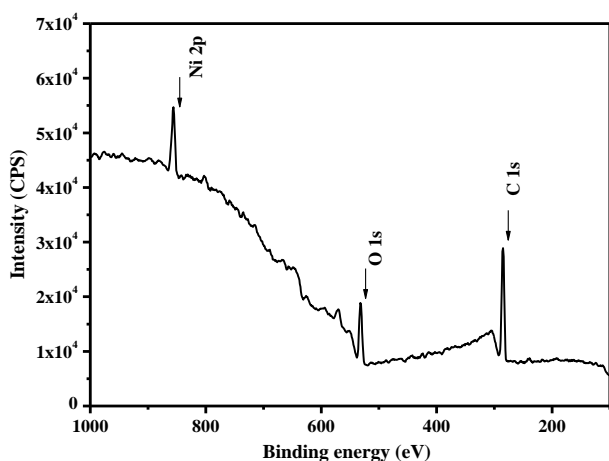
**Table 2** The crystallite size and lattice parameters of NiO thin films at various substrate temperatures

Substrate temperature (°C)	Orientation (hkl)	Crystallite size (nm)	Lattice parameter (nm)
30	(200)	6.1	0.421
100	(220)	7.3	0.419
200	(220)	8.2	0.419
300	(220)	9.1	0.420
400	(220)	10.3	0.423

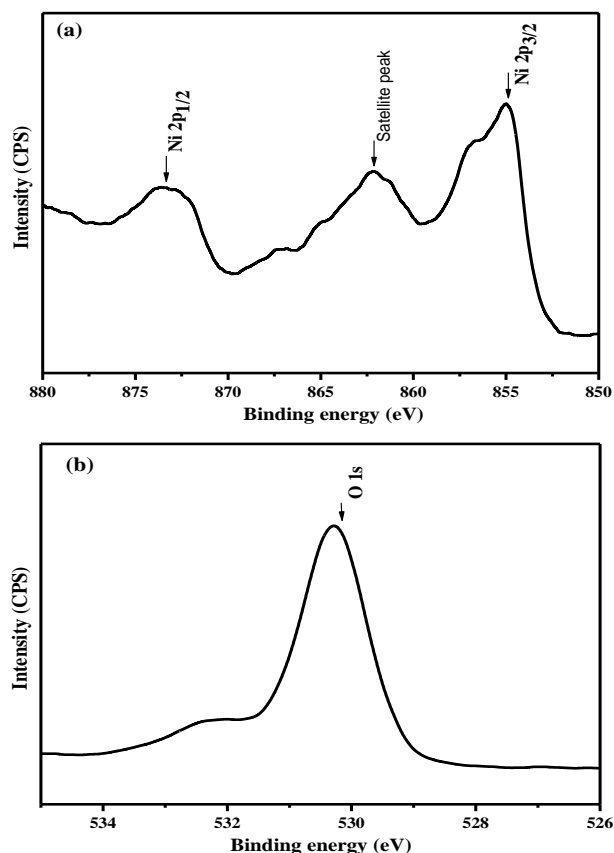
The lattice parameter of the films was also influenced by the substrate temperature. The variation in the lattice parameter with substrate temperature was due to the stresses developed in the films. The stress developed in the films was obtained by the shift in the interplanar spacing hence change in the lattice parameter. We observed that the crystallite size increased from 6.1 to 10.3 nm with preferred orientations by increasing the growth temperature.

##### 3.1.2 Chemical binding energy analysis

The chemical bonding states in the NiO films at various substrate temperatures were characterized by XPS analysis. Fig. 2 shows the XPS survey spectrum of NiO film at a substrate temperature of 200°C.

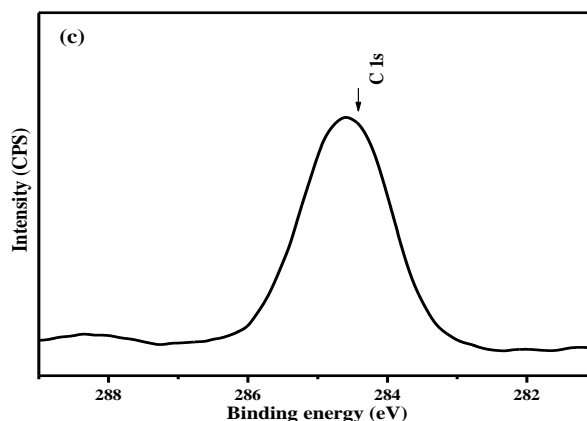


**Fig.2** XPS survey spectrum of NiO film at growth temperature of 200°C

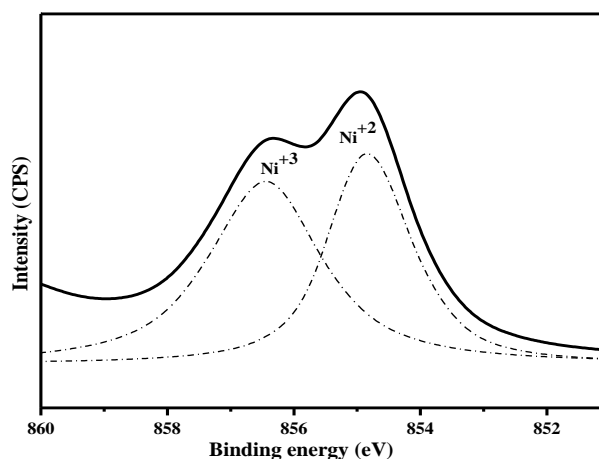


From this spectrum, the peak positions of C 1s, O 1s and Ni 2p<sub>3/2</sub> are at 284.2, 530.6 and 854.8 eV and were observed conspicuously at their respective standard values of the binding energies. Fig. 3(a) shows narrow scan XPS spectra of core-level binding energy of Ni 2p in the energy range 850 to 880 eV. This is in addition to the very broad peak at ~ 862.5 eV (in Fig. 3 (a)), which is the shake-up satellite peak of Ni<sup>2+</sup> and Ni<sup>3+</sup>. The core-level binding energies of 854.8 and 872.5 eV related to Ni 2p<sub>3/2</sub> and 2p<sub>1/2</sub> respectively. Fig. 3 (b) and (c) shows the narrow scan XPS

spectra of core-level binding energy of O 1s and C 1s in the binding energies at 530.4 and 284.5 eV respectively



**Fig.3** XPS narrow spectrum of (a) Ni 2p, (b) O 1s and (c) C 1s of NiO film at growth temperature of 200°C



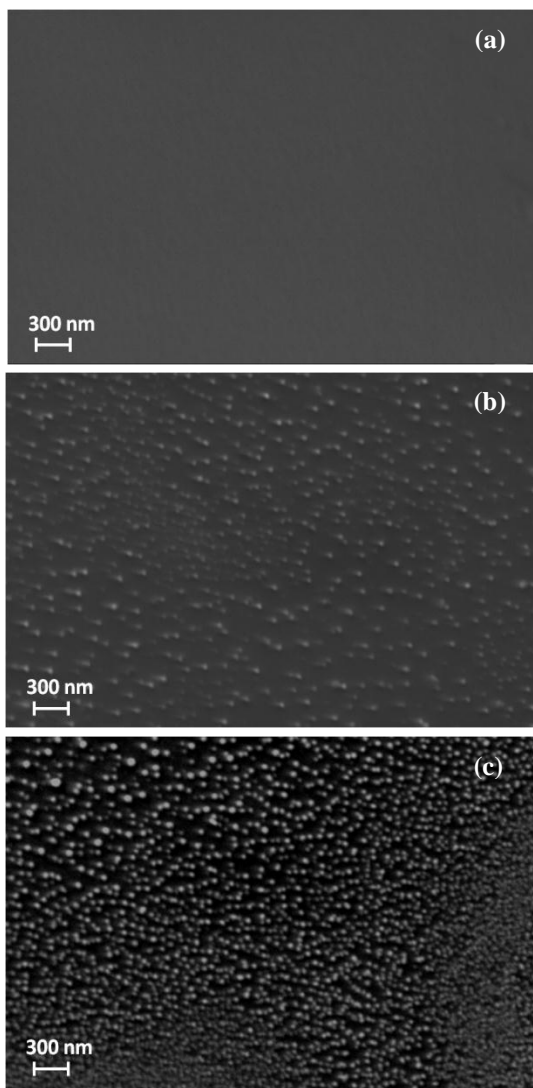
**Fig.4** Deconvolution for Ni<sup>3+</sup> and Ni<sup>2+</sup> of Ni 2p<sub>3/2</sub> peak of NiO film at growth temperature of 200°C

Further, the Ni 2p spectrum was deconvoluted into two component peaks and have been assigned to the Ni<sup>2+</sup> (NiO) and Ni<sup>3+</sup> (Ni<sub>2</sub>O<sub>3</sub>) respectively (Davidson, *et al*, 1996), (Hager, *et al*, 2009) (Fig. 4). The short dotted curves represent the deconvolution due to different components of nickel oxide films: NiO (854.8 eV) and Ni<sub>2</sub>O<sub>3</sub> (856.5 eV). The XPS spectra have been fitted by Gaussian curves corresponding to peaks of nickel oxide. These results were consistent with the previous reports of the composition and chemical states investigated by the XPS spectra of Ni 2p<sub>3/2</sub> in nickel oxide thin films deposited by reactive magnetron sputtering (Hotovy, *et al*, 1998), (Lee, *et al*, 2004), (Grosvenor, *et al*, 2006). The XPS studies revealed the grown films exhibited single phase of NiO.

### 3.2 Surface morphology and compositional analysis

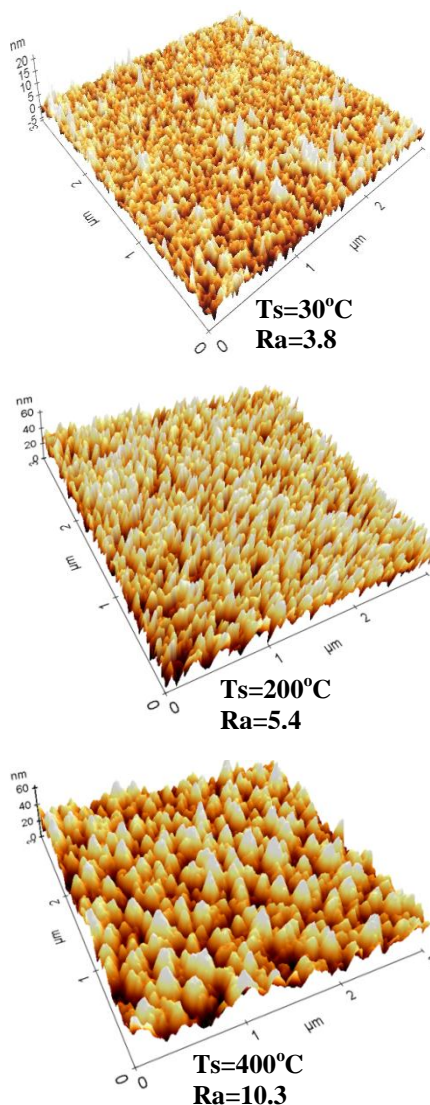
The variation of morphology with substrate temperature was observed by SEM (Fig. 5). It was observed that the films deposited at room temperature have smooth surface and fine grains appeared when the films formed at a

growth temperature of 200°C. When the films deposited beyond this temperature the size of the grains increased. By increasing the substrate temperature, the energy of the surface atoms increased which enhanced the mobility and improves the quality of film crystallinity.



**Fig.5** SEM images of NiO films at various substrate temperatures (a) 30°C, (b) 200°C and (c) 400°C

The atomic force micrographs of NiO films deposited at various substrate temperatures are shown in Fig. 6. The morphology of the films markedly varied with substrate temperature. The AFM micrograph of NiO films deposited at 30°C showed small islands which are homogenous and uniform indicating the amorphous nature in the films. As the substrate temperature increased to 400°C, the RMS roughness of the films was increased. Applying substrate temperature to the substrates increases ion bombardment, reducing the nucleation energy and giving rise to the variations in the surface morphology and microstructures of the thin films. Therefore suitable substrate temperature causes a surface energy which improves the morphology of the growing films. The RMS roughness of NiO films increased from 3.8 to 10.3 nm with the increase of substrate temperature from 30 to 400°C.

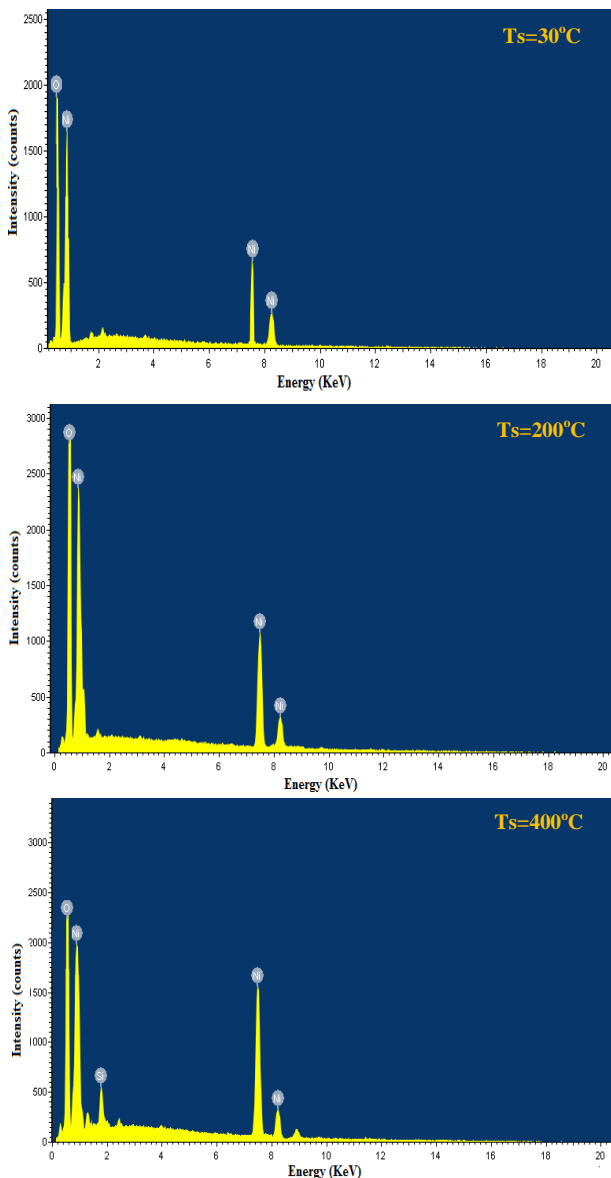


**Fig.6** AFM images of NiO films at various substrate temperatures

The energy dispersive spectroscopy (EDS) was employed to identify the composition of the deposited NiO films formed at different substrate temperatures. EDS results confirmed that all the deposited films consist of nickel and oxygen and the composition of the nickel gradually increased as substrate temperature increased (Fig. 7). It was resulted due to reduced amounts of oxygen as the temperature increased. The detailed elemental composition is given in Table 3.

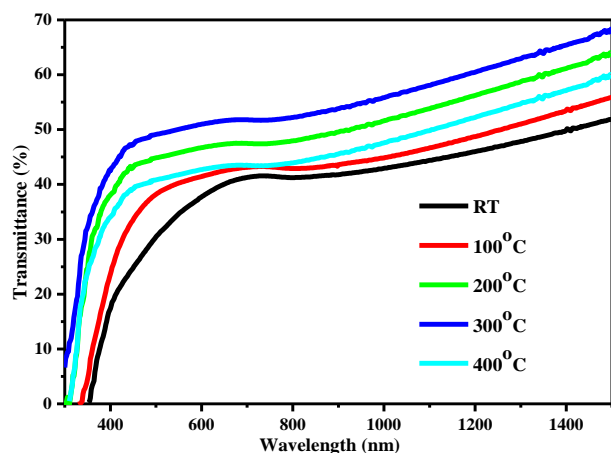
**Table 3** The elemental composition analysis of DC reactive magnetron sputtered NiO films at various substrate temperatures

Substrate temperature (°C)	Atomic %	
	Ni	O
30	49.27	51.73
100	51.28	49.72
200	52.04	48.96
300	53.89	46.11
400	54.93	45.07



**Fig.7** EDS profiles of NiO films at various substrate temperatures

3.3 Optical properties



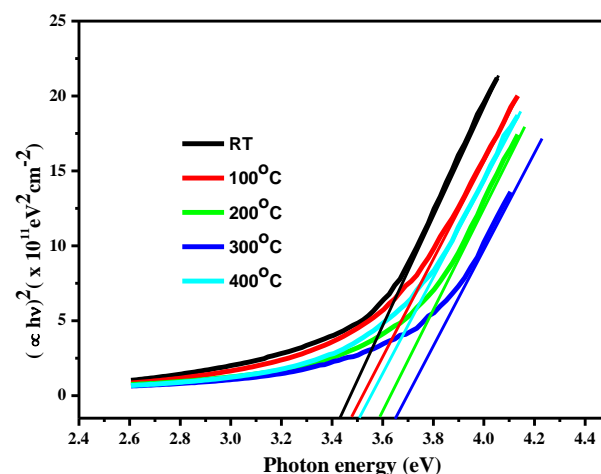
**Fig.8** Optical transmittance spectra and of NiO films at various substrate temperatures

The optical transmittance (T %) of the films was studied in the wavelength range 300–1500 nm at room temperature with unpolarised light at normal incidence. The transmission spectra of NiO films formed at various substrate temperatures in the range 30–400°C is shown in Fig. 8. The transmittance increased slightly with the increase of substrate temperature up to 300°C. As the substrate temperature is increased the density of defect centers decreases thereby increasing in the optical transmittance. However, on further increasing the substrate temperature to 400°C, the transmittance of the films decreased due to increase of Ni content.

The optical absorption coefficient ( $\alpha$ ) was evaluated using  $\alpha = (\ln T^{-1})/t$ , where t is the film thickness and T is the transmittance of the films (Chopra and Das, 1983). The best linear relationship is obtained by plotting  $(\alpha hv)^2$  against hv by the following relation,

$$\alpha hv = A (hv - E_g)^{n/2} \tag{2}$$

where  $\alpha$  is the absorption coefficient, A is a constant (independent from  $\nu$ ) and n is the exponent that depends upon the quantum selection rules for the particular material. The optical band gap values are obtained by extrapolating the tangential line of the data to the abscissa axis in the plot of  $(\alpha hv)^2$  as a function of hv. The direct band gap for the films increased from 3.43 to 3.65 eV with the increase of substrate temperature from 30 to 300°C. The increase of optical band gap with substrate temperature was due to the improvement in the packing density and increase in the crystallinity of the films (Fig. 9). However, on further increasing the substrate temperature (400°C), the optical band gap of NiO films decreased to 3.5 eV. This widening of the optical band gap with substrate temperature was due to the shift in absorption edge and also increased in carrier concentration.



**Fig.9** Plot of  $(\alpha hv)^2$  and  $(hv)$  of NiO films deposited at different substrate temperatures

3.4 Electrical properties

The electrical properties of NiO films as a function of growth temperature were analysed by Hall measurements.



The electrical resistivity ( $\rho$ ) was calculated by the following relation,

$$\rho = l/\sigma = VA/IL \quad (3)$$

where A is the cross-sectional area, L is the length between the potential probes, V is the measured voltage and I is the measured current. Electrical resistivity, mobility and carrier concentrations were carried out using Hall-effect on films of NiO in the temperature range 30–400°C. It was clear that the electrical properties of NiO thin films are greatly affected by substrate temperature. The room temperature (30°C) deposited films showed high electrical resistivity of 120.42  $\Omega$  cm. However, with increasing the substrate temperature to 400°C, it was gradually decreased to 0.023  $\Omega$  cm. The decrease in electrical resistivity was due to increase in carrier concentration.

**Table 4** Electrical information of DC reactive magnetron sputtered NiO films at various growth temperatures

Substrate temperature (°C)	Resistivity ( $\Omega$ cm)	Mobility ( $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ )	Carrier concentration ( $\text{cm}^{-3}$ )
30	120.42	0.8	$3.1 \times 10^{16}$
100	48.91	2.9	$1.6 \times 10^{17}$
200	13.24	4.5	$3.5 \times 10^{18}$
300	0.63	6.3	$8.9 \times 10^{19}$
400	0.023	8.1	$2.1 \times 10^{20}$

The Hall mobility measurements indicated that the films were p-type conduction. With increasing the substrate temperature from 30 to 400°C, the mobility of the films increased from 0.8 to 8.1  $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ . The carrier concentration of the films also increased from  $3.1 \times 10^{16}$  to  $2.1 \times 10^{20}$   $\text{cm}^{-3}$ . The carrier concentration depends on both crystalline microstructures and surface chemical reactions during the sputtering process (Chen, et al, 2005). The values of resistivity, carrier concentration and mobility of each substrate temperature are listed in Table 4.

## Conclusions

Nickel oxide (NiO) thin films were deposited by DC reactive magnetron sputtering process at different substrate temperatures (30–400°C) in a pure oxygen atmosphere. The films exhibited better crystallinity and the grain size and roughness of the samples increased with increasing of Ts. The widening of the optical band gap with substrate temperature was observed due to the shift in absorption edge and also increased in carrier concentration. The resistivity decreases with increase of substrate temperature. In this investigation, the lowest resistivity 0.023  $\Omega$  cm was obtained at high Ts. Finally, it was concluded that the growth temperature plays a key role in controlling the structural, morphological, optical and electrical properties of the NiO films.

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