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# Growth and Characterization of Electroplated NiO Coatings

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***Abstract:*** *Thin films of NiO have been prepared using potentiostatic electrodeposition technique from an aqueous electrolytic bath containing $NiSO_4$. Deposited films have been characterized using x-ray diffraction, scanning electron microscopy and energy dispersive analysis by x-rays. X-ray diffraction patterns showed that the prepared films possess polycrystalline nature with face centered cubic structure. Surface morphology and film composition showed that films with better stoichiometry and smooth surface are obtained at optimized growth condition. Optical absorption analysis showed that the prepared films possess direct band gap value around 3.46 eV.*

*Keywords: NiO; thin films, electrodeposition; x-ray diffraction; optical absorption analysis*

## 1. INTRODUCTION

Metal Oxides have attracted many researchers due to their combination of physical and chemical properties, which make them interesting for numerous research fields such as electrochemistry, catalysis, corrosion, spintronics and optoelectronics [1-6]. Among them, Nickel Oxide (NiO) is an extensively studied material, which exhibits semiconducting and electrochromic properties [1,7,8,9]. NiO is a material of interest for a variety of practical applications, such as electrochromic devices with good electrochemical stability, cyclic durability [10], catalysis [11], magnetic materials [12], gas sensors [13], fuel cells [14], catalyst for oxygen evolution [15], smart windows [16], and light emitting devices [17]. Thin films of NiO are usually crystallized in cubic structure with lattice constant a= 4.176 Å. There are a number of methods that have been adopted to prepare NiO thin films such as sputtering [18], sol gel technique [10], spray pyrolysis [19] and chemical bath deposition [20]. Purusothaman and Muralidharan have obtained NiO thin films using sol-gel technique and analyzed their structural, optical and electrochromic properties using x-ray diffraction, UV-VIS-NIR spectroscopy and cyclic voltammetric techniques, respectively [10]. NiO thin films were prepared using magnetron sputtering and their properties are investigated using x-ray diffraction, scanning electron microscopy and transmission electron microscopy by Magana and his co-workers [18]. NiO thin films have been obtained using spray pyrolysis technique and their properties were investigated by Reguig and his research group [19]. Hou and his coworkers [20] have prepared NiO thin films by chemical deposition technique and investigated their properties using x-ray diffraction, scanning electron microscopy, x-ray photoelectron spectroscopy, fourier transform interferometric techniques, respectively. Of all the physical and chemical deposition techniques used, electrodeposition is an attractive method for the preparation of unary, binary and ternary alloy thin films for a variety of applications, due to its low synthesis cost, no need of vacuum facility, no contamination to the surrounding, low temperature processing, control of growth rate and morphology by readily adjusting the deposition parameters as well as composition of the electrolytic bath [21-24].

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In the present study, thin films of NiO have been obtained on indium doped tin oxide coated conducting glass (ITO) substrates using potentiostatic electrodeposition technique. Surface profilometer analysis has been carried out to determine the thickness of the deposited films. Prepared films were subjected to x-ray diffraction, scanning electron microscopy, energy dispersive analysis by x-rays and optical absorption techniques, respectively. The effect of film thickness on structural, morphological, compositional and optical properties of the deposited films was analyzed and the results are reported.

## 2. EXPERIMENTAL DETAILS

The chemicals used in the present work were of AR grade reagents. NiO thin films were grown using electrodeposition technique with the help of a SP50 Potentiostat/Galvanostat (Bio Logic, France). The working solution was obtained by dissolving 0.8426 g of $NiSO_4$ in 100 cc double distilled water and 50 cc of the dissolved solution was used as an electrolytic bath for all depositions. Initially the pH of the electrolytic bath was 4.5 ± 0.1 and by adding an adjustable amount of KOH the pH of the electrolytic bath was increased to 10.5 ± 0.1 and this could be used as optimized pH value for all depositions. The depositions were carried out with the help of potentiostat/galvanostat unit using three electrode cell configuration with ITO substrate as the working electrode, platinum electrode as counter electrode and a saturated calomel electrode (SCE) as reference electrode, respectively. Before utilized for deposition ITO substrates were treated for 10 minutes in a bath of isopropanol and then rinsed with acetone. The SCE was positioned close to the working electrode with the help of luggin capillary arrangement. The deposition potential was fixed as - 800 mV versus SCE for all depositions. The bath temperature was fixed as 75°C for all depositions. The deposition time was found to vary in the range between 5 and 70 minutes to obtain films with various thickness values.

The thickness of the deposited films was measured using a Stylus Profilometer (Mitutoyo SJ 301, Japan). X-ray diffraction data of the prepared films was determined using an x-ray diffractometer (XPERT PRO PANalytical, Netherland) with $CuK_\alpha$ radiation with wavelength value around 1.5406Å. Structural parameters such as crystallite size, strain and dislocation density were determined using the x-ray diffraction data. Morphology and film composition of the deposited films were analyzed using an energy dispersive analysis by x-rays set up attached with the scanning electron microscope (Philips Model XL30,USA). Optical absorption analysis was carried out with the help of a UV-VIS-NIR spectrophotometer (Shimadzu Model 2600, Singapore).

## 3. RESULTS AND DISCUSSION

### 3.1. Film Thickness

Growth of NiO thin films on ITO substrate is controlled by separate variables such film thickness, uniformity and surface morphology [22,23]. We have obtained films of various thicknesses by controlling the plating current and by adjusting the deposition time. Figure 1 shows the variation of film thickness with deposition time for films obtained at different deposition times and at the bath temperature 75ºC. It is observed that the value of film thickness increases with deposition time and reaches its maximum value at a deposition time of 50 minutes, afterwards the thickness value decreases slightly which is indicated in figure 1. This may be due to the population of adatoms on film surface during deposition resulting in increased value of nucleation rate, corresponding to higher value of thickness for the deposited films. Since, saturated value of film deposition is obtained at limited value of current plateau thus leads to higher value of film thickness on cathode at a deposition time of 50 minutes. At lower bath temperature such as below 50ºC an irregular growth with rough surface is obtained, whereas at higher bath temperature such as 75 ºC (above 50 ºC) films with higher thickness and smooth surface is obtained. Further increasing bath temperature above 75 ºC, there is peel off of film from the substrate. Therefore, bath temperature and deposition time are fixed as 75ºC and 50 minutes in order to get films with higher thickness and better quality.

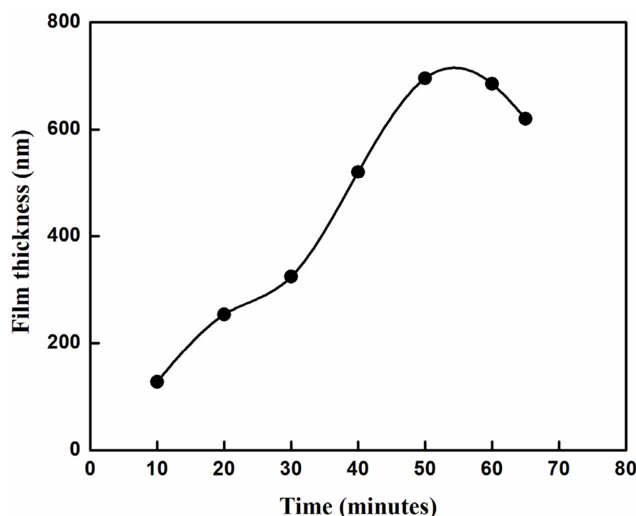


Figure 1. Variation of film thickness with deposition time for NiO thin films obtained at bath temperature 75ºC.

### 3.2. X-ray Diffraction

X-ray diffraction analysis has been carried out to determine the crystalline nature and phases of the deposited films. The films prepared at lower bath temperatures, such as below 50°C, are found to be less adherent to the substrate. At higher bath temperatures, such as above 75°C, there is peel off of film from the substrate. As a result, the bath temperature is fixed as 75°C to obtain films with higher thickness and better crystallinity. Figure 2 shows the x-ray diffraction pattern recorded for NiO thin films prepared at bath temperature 75°C. The diffraction peaks of NiO are found at angles of 32.33, 43.16, 62.55, 73.62 and 76.02 corresponding to the lattice planes (111), (200), (220), (311) and (222) respectively. The observed peaks in the diffractogram are indexed and the corresponding values of lattice spacing “d” were calculated and compared with standard JCPDS ICDD file for cubic NiO [25]. X-ray diffraction pattern showed that the deposited films possess polycrystalline nature with face centered cubic structure with lattice constant (a = b = c = 4.1556 Å) with most prominent reflection along (200) direction. Crystallite size is defined as the sizes of crystallites formed on surface of the substrate. The crystallite size of the deposited films

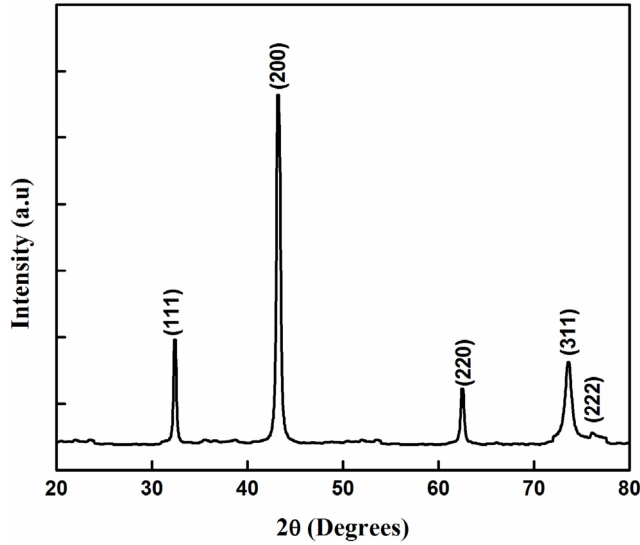


Figure 2. X-ray diffraction pattern recorded for NiO thin films obtained at bath temperature 75 ºC.

has been estimated using FWHM data and Debye-Scherrer formula (eq.(1)) [22].

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad (1)$$

where, λ is the wavelength of $CuK_\alpha$ target used (λ=1.540 Å), β is the full width at half maximum of the peak in radian, θ is the Bragg's diffraction angle at peak position in degrees. The deposition time is found to vary in the range between 5 and 70 minutes, we have obtained films with different thickness and crystallite size values. Variation of crystallite size and strain with film thickness for films obtained at different deposition times is shown in figure 3a. It is observed that the value of crystallite size is observed to increase if the film thickness value increases upto 760 nm, thereafter its value decreases slightly.

Strain is defined as the restoring force acting on the surface of the film to restrict the formation of crystallites on its surface [21]. The value of strain is calculated using eq.(2). It is also observed that the value of strain is found to decrease and reaches its minimum value at film thickness value around 760 nm, afterwards its value increases slightly. Dislocation density is defined as the number of dislocation lines per unit volume of the crystal and it can be calculated using eq.(3) [21,22]. Variation of dislocation density with film thickness for NiO thin film is shown in figure 3b. It is observed that the value of dislocation density is found to decrease with film thickness and reaches its minimum value for film with thickness value 760 nm, afterward its value increases. Maximum value of crystallite size, minimum value of strain and dislocation density are obtained for films with higher thickness value around 760 nm. Similar functional dependency of microstructural parameters with film thickness for $FeSe_2$ thin films has been reported earlier [26].

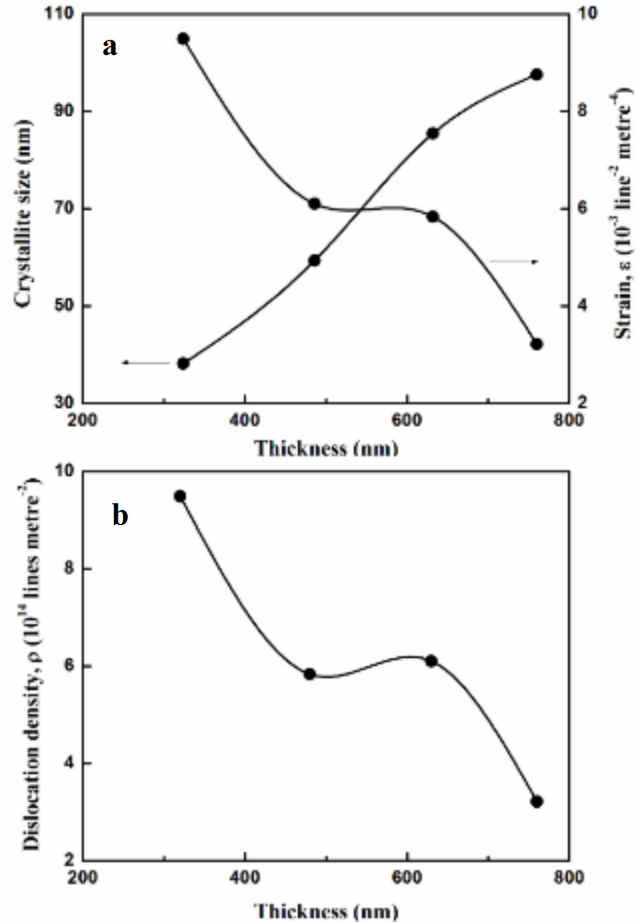


Figure 3. a. Variation of crystallite size and strain with film thickness for NiO thin films obtained at bath temperature 75ºC.
b. Variation of dislocation density with film thickness for NiO thin films obtained at bath temperature 75ºC.

$$\beta = \left[\frac{\lambda}{D\cos\theta} - \varepsilon \tan\theta\right] \quad (2)$$

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

### 3.3. Surface Morphology and Film Composition

Surface morphology and film composition of the deposited films have been analyzed using energy dispersive analysis by x-rays set up attached with the scanning electron microscope. SEM picture of NiO thin films prepared at bath temperature 75°C is shown in figure 4a. It is observed that the deposited films possess hierarchical structure with uniformly distributed needle shaped grains. The sizes of the grains are found to be in the range between 0.45 and 0.75 μm. The average size of the grain was found to be 0.67 μm. Variation of film thickness with Ni and O content for films prepared at different deposition times is shown in figure 4b. It is observed that

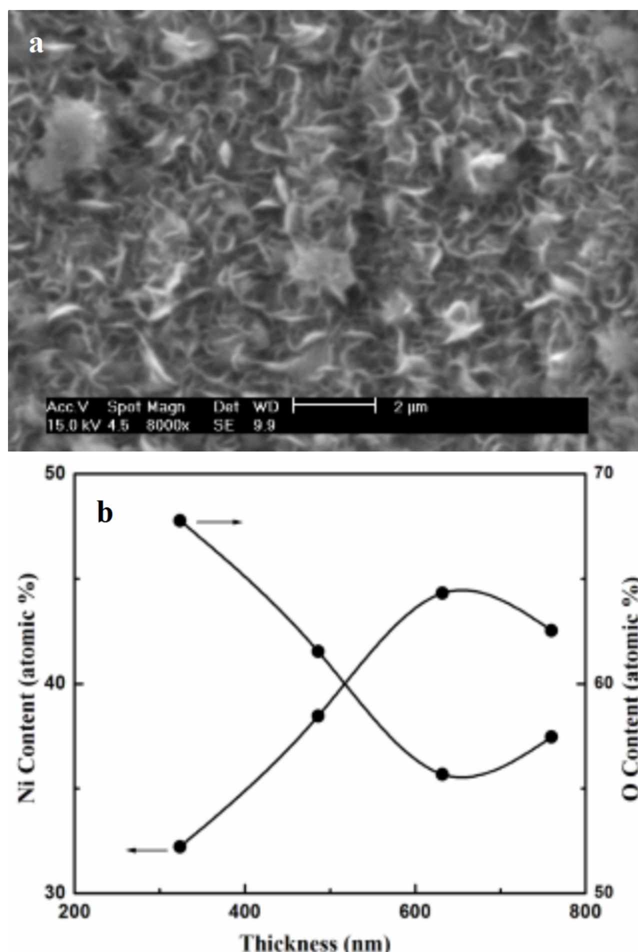


Figure 4. a. SEM image of NiO thin film obtained at bath temperature 75 ºC., b. Variation of Ni and O content with film thickness for NiO thin films obtained at bath temperature 75ºC.

the content of Ni increases and the content of O decreases if the value of film thickness increases from 320 to 760 nm, thereafter the content of Ni slightly increases. Therefore, films with better stoichiometry and higher thickness are obtained for films prepared at a deposition time of 50 minutes. The atomic molar ratio (Ni:O) for NiO thin films obtained at optimized higher film thickness value of 760 nm is 44.32:55.68 and it is approximately 0.8:1.This result is consistent with the results of x-ray diffraction analysis of the sample with phase corresponding to $Ni_{0.8}O_1$.

### 3.4. Optical Absorption Analysis

The optical absorption and transmittance spectra of NiO thin films prepared on ITO substrate at bath temperature 75°C was recorded in the wavelength range between 300 and 1100 nm. Any substrate absorption present was corrected by introducing an uncoated ITO substrate in the reference beam. The absorption coefficient (α) rises sharply owing to band-to-band transition and levels off later. An analysis of absorption spectrum in the energy range between 1.5 and 3.5 eV indicates that (α) follows the relation. The value of absorption coefficient was determined using the following

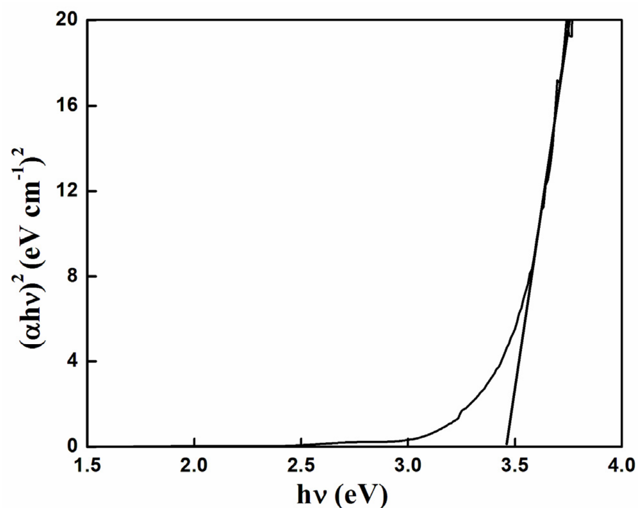


Figure 5. Plot of (hν) versus $(\alpha h\nu)^2$ for NiO thin films obtained at bath temperature 75 ºC.

eq.(4).

$$(\alpha) = \frac{A}{h\nu\left(h\nu - E_g\right)^{-1/2}} \qquad (4)$$

where, α is the absorption coefficient in $cm^{-1}$, hυ is the photon energy in eV, A is an energy dependent constant, which is related to the effective masses associated with valence band and conduction band, $E_g$ is the gap between the bottom of conduction band and top of valence band at the same value of wave vector. From the calculated value of absorption coefficient, a plot of (hυ) versus $(\alpha h\upsilon)^2$ is drawn for films obtained at bath temperature 75°C, which is shown in figure 5. Extrapolation of the linear portion of the graph to energy (hυ) axis gives band gap value of the material. The band gap value of the material is found to be 3.46 eV, which must be closer to band gap value of NiO thin films reported earlier [27].

## 4. CONCLUSIONS

Thin films of NiO were deposited on ITO substrates using potentiostatic electrodeposition technique. X-ray diffraction analysis revealed that the prepared films possess polycrystalline nature with cubic structure and preferential orientation along (200) plane. Structural parameters such as crystallite size, strain and dislocation density were determined using XRD data and its dependency showed that the parameters exhibit monotonic variation with film thickness for films obtained at different deposition times. The surface morphology showed that the prepared films exhibit smooth surface covered with needle shaped grains. Film composition revealed that films with well defined stoichiometry was obtained at the optimized bath temperature of 75°C. Optical absorption analysis showed that the deposited films possess direct band gap value around 3.46 eV, which must be quite close to the value reported earlier.

## 5. ACKNOWLEDGEMENT

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