INFLUENCE OF DEPOSITION TIME ON THE PROPERTIES OF CHEMICAL BATH DEPOSITED NICKEL OXIDE THIN FILMS

Thet Mar Win[1] and Pho Kaung[2]

Abstract

Nickel Oxide (NiO) thin films were synthesized on glass substrates from aqueous solution of nickel chloride hexahydrate ($NiCl_2.6H_2O$), potassium persulfate ($K_2S_2O_8$), ammonia in which ammonia was employed as complexing agents in the presence of hydroxyl solution. NiO thin films were prepared by Chemical Bath Deposition (CBD) method at different deposition time (60, 75 and 90) min. The structural, surface morphological and optical properties of 450 ºC- annealed NiO thin films were investigated. The XRD studies revealed that NiO thin films were polycrystalline nature with cubic structure. Surface morphology, average grain size and thickness of NiO thin films were estimated from different SEM micrographs. The optical absorbance and transmittance spectra of NiO thin films were recorded in the wavelength range 200 nm - 1100 nm. The sharp absorption peaks of all NiO films were observed at below 400 nm. It was found that NiO thin films with high transmittance in visible region. The refractive index, extinction coefficient and optical conductivity were calculated from the optical measurements. The direct optical energy band gap of 450ºC –annealed NiO films was found to be in the range 3.43 eV-3.76eV.

Keywords: Chemical Bath Deposition method, Deposition time, NiO thin films, Refractive index, Optical energy band gap

Introduction

Nickel oxide (NiO) is a versatile wide band gap semiconductor material. At present, transparent conducting oxide films, such as indium oxide, tin oxide and zinc oxide, are routinely used as transparent electrodes and window coatings for opto-electronic devices [Gopchandran K G et al., 1997 and Benny J et al., 1999]. These films are n-type. However p-type conducting films are required as optical windows for devices where hole injection is required. NiO is a p-type semiconductor with a band gap ranging from 3.6 eV to 4.0 eV, transparent to ultraviolet (UV), visible and near infrared radiation and consequently has the potential to address this need [Sasi B et al., 2003].

There are several methods for synthesis of NiO thin films on various substrates including physical as well as chemical deposition methods. The physical methods used are DC reactive magnetron sputtering and RF sputtering while chemical methods used to deposit NiO thin films are vapor deposition, chemical bath deposition, sol-gel, electro deposition and spray pyrolysis [**Chena H L et al., 2005].**The optical properties of thin films are very important for many applications including interference devices such as antireflection coatings, laser mirrors and monochromatic filters as well as optoelectronics, integrated optics, solar power engineering, microelectronics and optical sensor technology depending on the reflectance and transmittance properties of the films during their preparation. The optical constants of thin films provide us the information concerning with microscopic characteristics of materials [Safwat A M et al., 2011].

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The chemical bath deposition (CBD) method was used in this work to deposit NiO thin films on the glass substrate due to its simplicity and versatility. The effect of deposition time on the structural, surface morphology and optical properties of NiO thin films was evaluated.

Experimental Procedure

The phase formation of chemically deposited NiO thin films for different deposition time were characterized by X- ray diffraction technique using Rigaku Smart Lab X-ray Diffractometer with Cu-K_α radiation (λ = 1.5404 Å) operating at 40 kV and 40 mA. Surface morphology and thickness of NiO thin films were examined by Scanning Electron Microscopy (SEM) taken by JEOL- JCM 6000 Plus. The optical properties of the films were recorded by Schimadzu UV-Vis (UV-1800) spectrophotometer in the wavelength range of 200 nm-1100 nm.

Preparation of the Glass Substrates

The microscopic glass substrates (2.54 cm × 2.54 cm) were put into a beaker containing distilled water and kept for 10 minutes to remove contaminants such as dust on their surfaces. Then the substrates were degreased by hydrochloric acid for 1 hour and rinsed with distilled water and dried in air for a few minutes. Then, the glass substrates were slid into paper-poster plastic hangers.

Nickel Oxide Thin Films Grown by CBD Method

To synthesis the NiO thin films, high purity nickel chloride hexahydrate ($NiCl_2.6H_2O$) is used as source of Ni. A precursor solution is prepared by using 80 ml of 1M $NiCl_2.6H_2O$, 60 ml of 0.1M $K_2S_2O_8$, and 20 ml of aqueous ammonia (25-28%) in 200 ml beaker. The substrates were kept vertically in the deposition bath with constant stirring at 70°C. The deposited films are extracted from deposition bah after 60 min, 75min and 90 min. Then washed with distilled water in order to remove loosely bounded particles and further annealed at 450 °C in air for 2 hour to be uniform and well adherent to the substrate.

Results and Discussion

Structural Analyses

The X- ray diffractograms of 450 ºC -annealed NiO thin films for different deposition time were shown in Fig 1. The peaks (111), (200) and (220) were observed at 2θ values 37.238°, 43.310° and 62.851° for film NiO-1 (60 min), 37.191°, 43.337° and 63.029° for the film sample NiO-2 (75 min) and 37.224°, 43.301° and 62.795° for NiO-3 (90 min) films, respectively. All NiO films were found to have polycrystalline nature and bunsenite phase with cubic structure with the preferential orientation along the (200) plane. This conforms to standard card number JCPDS 71-1179.

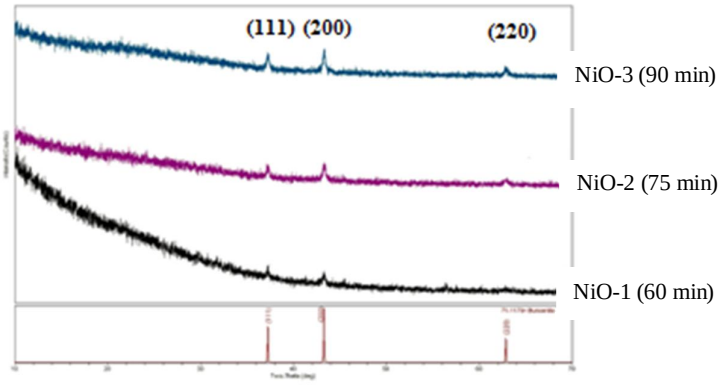


Figure 1 XRD patterns of 450 ºC -annealed NiO thin films for different deposition time

The average crystallite sizes (D) were determined Debye Scherrer's formula,

$$D = \frac{K\lambda}{\beta\cos\theta}$$

where, the constant K is a dimensionless constant often called the shape factor with a value of 0·94, λ the wavelength of X-ray used which is CuK_α radiation (λ = 1.54 Å), β the full width at half maximum of the diffraction peak and θ is the diffraction angle. It was observed that the crystallite size of the NiO film was improved with increasing deposition time. The dislocation density (δ) which represents the amount of defects in the film was determined from the formula,

$$\delta = \frac{1}{D^2}$$

where "δ" the dislocation density and "D" is the crystallite size.

The micro strain (μ) produced in the NiO thin films was calculated by using the formula,

$$\mu = \frac{\beta\cos\theta}{4}$$

The occurrence of micro strain may be attributed to stretching and compression in the lattice. The lattice constant "a" for the cubic structure is given by the relation,

$$\frac{1}{d^2} = \frac{(h^2+k^2+l^2)}{a^2}$$

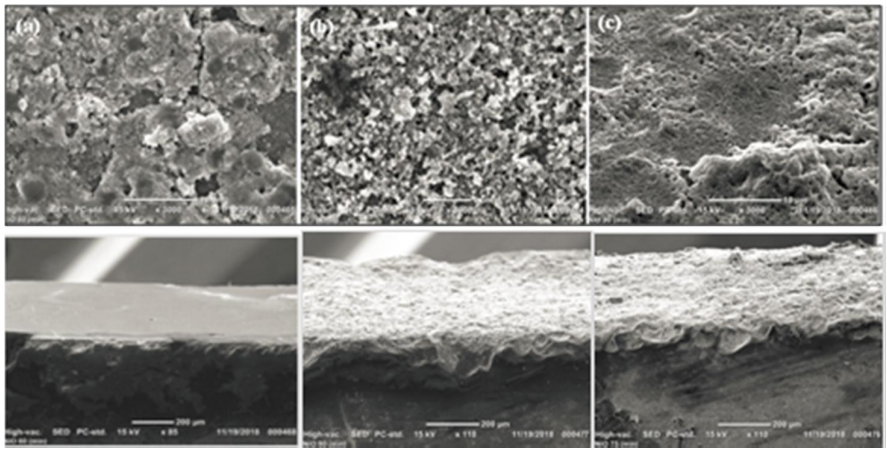
where "d" is the inter-planer distance and (hkl) are the Miller indices. Structural parameters of 450 ºC - annealed NiO thin films for different deposition time were presented in Table 1. The peak broadening decreases and the sharpness of the peak increases which clearly denote the reduction of lattice strain and increase in crystallinity of 450 ºC - annealed NiO films.

Surface Morphology and Thickness Measurement of NiO Thin Films

The SEM micrographs of 450 ºC -annealed NiO thin films for different deposition time were depicted in Fig 2. There was a distinct change in surface morphology for films by increasing deposition time. Flake surface morphology was observed in NiO-1 (60 min) film. The surface of NiO-2 (75 min) film sample was evenly covered with homogeneous grains with little

pores. The SEM micrograph of NiO-3 (90 min) film revealed inhomogeneous cellular like morphology. The surface morphology strongly depends on deposition time, concentration, orientation of grain growth and nucleation process.

Thickness of the film plays an important role in determining the film properties. Thickness of the NiO thin films were measured by SEM through the cross- section of the sample using imaging software. The average grain size and estimated thickness values are presented in Table 1.



(a) (b) (c)

Figure 2 Surface morphology (upper) and cross sectional view (lower) SEM images of 450ºC - annealed NiO thin film for deposition time (a) 60 min (b) 75 min and (c) 90 min

Table 1 Structural parameters of 450 ºC - annealed NiO films for different deposition time

Sample	NiO-1	NiO-2	NiO-3
Deposition Time (min)	60	75	90
Film Thickness (μm)	264	353	378
Average Lattice Constants (a=b=c)(Å)	4.1774	4.1747	4.1793
System	Cubic	Cubic	Cubic
Intense Peak (hkl)	(200)	(200)	(200)
FWHM ($\times 10^{-3}$ rad)	7.69	6.82	5.22
Crystallite Size from XRD(nm)	20.2	22.8	29.9
Dislocation density ($\times 10^{16}$ lines/ m^2)	0.24	0.19	0.11
Microstrain ($\times 10^{-3}$)	1.79	1.59	1.21
Average Grain Size from SEM(μm)	0.77	0.23	0.12

Optical Properties

Energy band gap and index of refraction are the two fundamental properties that determine the optical and electrical and electronic properties of semiconductors. The energy gap is determined by threshold of photon absorption while refractive index is a measure of transparency of the material to the incident light. The variation of absorbance and transmittance

spectra with wavelength of annealed NiO films for different deposition time 60 min, 75 min and 90 min was shown in Fig 3(a) and 3(b), respectively. The absorbance decreases rapidly at short wavelengths corresponding to the energy gap of the film. This evident increase of energy is due to the interaction of the material electrons with the incident photons which have enough energy for the occurrence of electron transitions. The sharp absorption edges were observed at 297 nm, 298 nm and 303 nm for NiO-1 (60 min), NiO-2 (75 min) and NiO-3(90 min) films. For a transmittance study, all NiO thin films showed transmittance of ~ 84 %, ~27 % and ~19 %, in the wavelength range of visible region, respectively.

The energy band gap value of NiO thin films was determined using the absorbance spectra in the wavelength range 300 nm- 900 nm. Absorption coefficients (α) have been evaluated using absorbance (A) data and following equation:

$$\alpha = 2.303\frac{A}{t}$$

where "t"is film thickness (μm). The optical absorption gives the relationship between the absorption coefficient "α" and the photon energy "hν" as

$$\alpha = \frac{B(h\nu - E_g)^{\frac{1}{2}}}{h\nu}$$

where "B" is a constant called the band tailing parameter. The band gap values were determined from the intercept of the straight line portion of the square of absorption coefficient $(\alpha h\nu)^2$ is plotted as a function of photon energy (hν) were shown in Fig 4. The direct energy band gap value of NiO-1 (60 min), NiO-2 (75 min) and NiO-3 (90 min) found to be 3.43 eV, 3.62 eV and 3.76 eV, respectively.

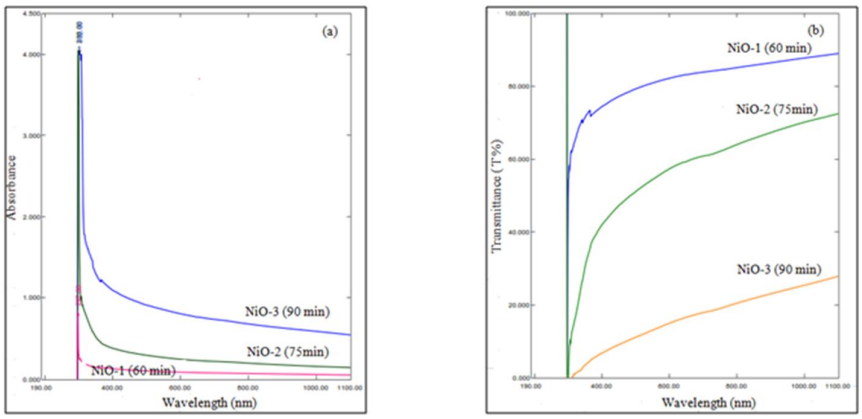
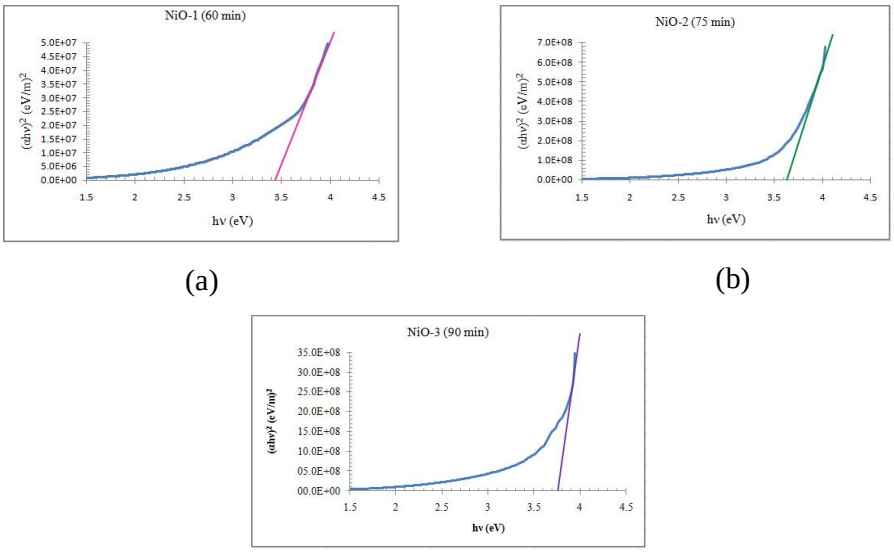


Figure 3 (a) The absorbance and (b) transmittance spectra of NiO films for deposition time (60,75 and 90) min



(a) (b)

(c)

Figure 4 Variation of $(\alpha h\nu)^2$ with photon energy of 450ºC -annealed NiO thin film for deposition time (a) 60 min (b) 75 min(c) 90 min

The optical constants such as refractive index (*n*) and the extinction coefficient (*k*) and optical conductivity (σ) were evaluated from the reflectance data over the spectral range from 300 to 1100 nm.

The reflectance has been found by using the relationship:

$$R + T + A = 1$$

The "*n*" and "*k*" have been and using the following relations,

$$n = \frac{1+\sqrt{R}}{1-\sqrt{R}}$$

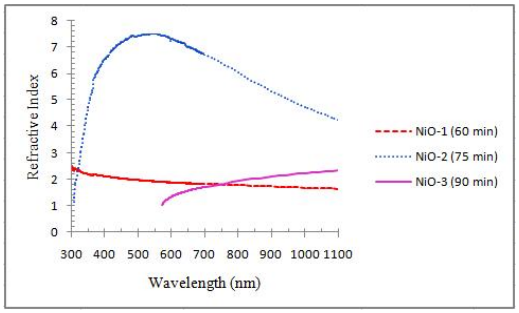
$$k = \frac{\alpha\lambda}{4\pi}$$

The optical conductivity "σ" was determined using the following equation

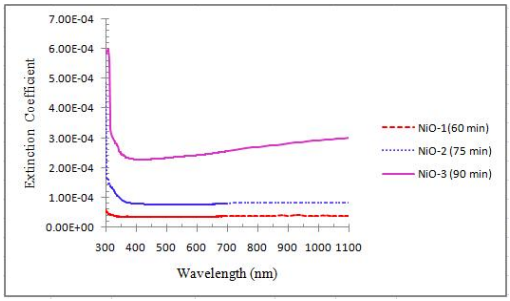
$$\sigma = \frac{\alpha nc}{4\pi}$$

where "*c*" is the velocity of light. The variation of refractive index with wavelengths of the NiO films for different deposition time is shown in Fig 5(a). NiO-1 thin film, it can be seen that the maximum index of refraction (n = 2.49 at λ = 302 nm, strong absorption region) and the *n* values between 2.49 and 1.82 was observed in the visible region. The NiO-2 thin film sample showed an anomaly. It was observed that the value of refractive index 1.29 - 3.53 at the wavelength range 308 nm - 334 nm. The *n* value drastically increased in the wavelength range 380 nm - 660 nm and then abruptly decreases in the wavelength range 680 nm -1100 nm. For NiO-3 thin film, the index of refraction (n= 1.021 at λ=570 nm) was observed. And then the *n* value is gradually increasing and reaching to the value of 1.71- 2.33 in the wavelength range 700 nm- 1100 nm.

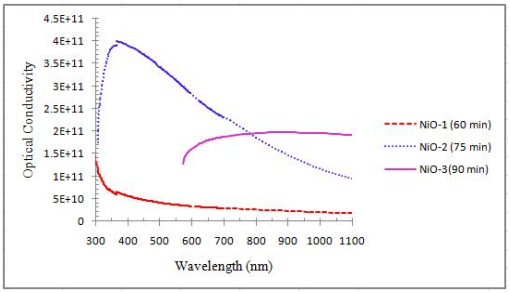
Fig.5 (b) shows the variation of extinction coefficient (*k)* as a function of wavelength (*λ)* of NiO films for various deposition time. It was observed that the *k* value 0.62 $\times 10^{-4}$, 4.95 $\times 10^{-4}$ and 5.83 $\times 10^{-4}$ at λ =300 nm for NiO-1, NiO-2 and NiO-3 thin films. The *k* value decreases rapidly at short wavelength 300 nm- 400 nm and after that the value of *k* remains almost constant. The rise and fall in the value of *k* is directly related to the absorption of light. The variation of optical conductivity (σ) with wavelengths of NiO films for different deposition time was shown in Fig 5 (c). It was noticed that the σ value increases rapidly beyond absorption edge region because of the high increase of the absorbance in this region.



(a)



(b)



(c)

Figure 5 Variation of (a) refractive index (b) extinction coefficient (c) optical conductivity with wavelength of NiO thin films for different deposition time

Conclusions

The role of deposition time in NiO thin films were prepared by CBD method and all these films were annealed at 450 ºC for 2 h. The XRD studies revealed that NiO-1(60 min), NiO-2 (75 min) and NiO-3 (90 min) thin films were polycrystalline nature with cubic structure. Defects decreases by the increasing of thickness which means the increasing of crystallite size of NiO thin films. From SEM micrographs, the surface morphologies were transformed from flake shaped morphology to homogeneous grains and to inhomogeneous cellular like morphology. It was found that the grain sizes were decreased as deposition time increased.

The refractive index (*n)* value of NiO-1 film tends to decrease with increasing the wavelengths. The *n* values were observed between 2.49 and 1.82 in the visible region. This is due to the influence of lattice absorption. It was observed that the index of refraction increased

with wavelength of visible region in NiO-2 and NiO-3 thin films. It is due to the anomalous dispersion. The extinction coefficient value varies in UV range and it is almost constant in the visible and NIR range for all NiO films. The optical conductivity value of NiO films increases rapidly beyond absorption edge region because of the high increase of the absorbance in this region. The transmittance of NiO thin film decreases from 84 % to 19 % with increasing film thickness in the visible region. The direct energy band gap increases from 3.43 eV to 3.76 eV with deposition time, which is due to the smaller grain size. Having wide band gap and high transmittance, NiO thin films make them promising candidate for optoelectronic devices as well as window layer in solar cell applications.

Acknowledgements

We are grateful to Professor and Head Dr Khin Hla Hla Win and Professor Dr Cho Cho Moe, Department of Engineering Physics, Technological University (Thanlyin) for their kind permission to carry out this work.

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