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Research article

Effect thickness on structural and optical properties of NiO thin films

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ABSTRACT

In this research, NiO thin film were prepared by chemical spray pyrolysis technique, using $NiO(NO_3)_2$, on glass substrates preheated at (350°C) with spray rate 3sec./1min , with different thickness (0.25 – 0.5 – 0.75 – 1.0 – 1.25 μm) . The investigation of (XRD) indicates that the (NiO) films are polycrystalline type of (cubic), XRD results and grain size obtained increased with thickness. The optical properties such as transmittance spectra of NiO film were collected between 300 to 850nm wavelength. Optical functions of these films were of homogenous structure and the results agree with reported data obtained uising different methods of film deposition, and their results obesults observed that the increase in thickness caused improved in structural and optical properties generally.

Key words: thin film, NiO, thickness, structural, optical, chemical spray pyrolysis.

1. INTRODUCTION

Nickel oxide (NiO) is a transition metal oxide with excellent chemical and thermal stabitiy [1-3] It has potential application in such as electrochromic display devices, absorber and as cathode material for alkaline batteries quite reasonable for possible switching applications [2-5].

Some Other interesting electronic properties of NiO thin film include its wide band gap range of 3.6 - 4.0 eV [6] and its p-type conductivity which make it favorable material for material for electronic device applications [7-8] .

The film can be used for coating eye glasses for protection from sunburn caused by UV radiations. Since they show moderately high VIS-NIR transmittance it can be used for coating of poultry roofs and walls. This will ensure that young chicks which have not developed protective thick feather are protected from UV radiation while the heating of the poultry house is maintained by the heating portion of the heating portion of the electromagnetic spectrum, and as well allows for admittance of visible light in the house [9].Electrochromic devices have also been considered by NASA in hope of replacaing the Venetian blind radiators in future satellites [10] .

The most important potential commercial of the electrochromic films would be: glazing of buildings and houses to provide dynamical control of the incoming illumination [11] and thus an energy efficient housing and lifestyle [12]. NiO plays an important role in the because of its anode electrochromic.

There are a number of physical and chemical routes for preparing thin film , like pulsed laser deposition , ion beam sputtering , thermal evaporation , vacuum deposition chemical vapor deposition , sol-gel , deposition bath chemical etc [9-13] . The Chemical Spray pyrolysis (CSP) technique is a better chemical method at a lower cost for the preparation of thin films with a larger area. The flow rate of carrier gas , the concentration of pressure and types of reducing agents on the size , morphology and crystallinity of nanoparticles nanoparticles [15] developed a mathematical model for the evaporation of the micro and nanosize solution droplets . The model is used to predict whether the particles are fully filled or hollow .In the CSP technique , various parameters like air pressure deposition rate, substrates temperature , distance between nozzles to substrate ,cooling rate deposition also affect the physical , electrical and optical properties of thin films. The film properties are sensitive not to their structure but also to many other parameters including thickness, surface states , morphology etc [16]. The CSP technique has found to be useful for the preparation of metallic oxides , semi-conducting oxides, binary and ternary chalcogenides and superconducting thin films of various materials.

In this work , chemical spray pyrolysis technique was used for deposition of NiO thin films glass substrates at (350°C) and analyzed to understand the role of film thickness on structural and optical properties of the nickel oxide films. The thickness films was varied between 0.250 and 1.25 μm for different thickness .

2. Experiential Details

The preparation of NiO thin films glass slide was carried out using chemical spray pyrolysis technique, the glass substrates (25 × 25 ×1) mm^3 were previously cleaned in water with detergent , then immersed in ethanol to remove any oil , last but not least rinsed with distilled water and dried in air.

The precursor solution prepared by dissolving a certain amount (0.05 M) of nickel nitrate $Ni(NO_3)_2 .6H_2O$ (molecular weight 290.81 g/mol) in 50 ml of distilled water and several drops of HCL provide precipitation and increase clarity of the solution.

The glass substrates was kept at a temperature of (350°C) . The spray rate of (3 ml /min) was maintained using carrier gas is nitrogen compressor regulator (1.5 mbar) , the distance between spray nozzle and substrates was fixed at (28 cm) . The deposition process was repeated several times and reproducibility of the results until we get the required thickness . After deposition process was completed, the films were kept on the heater at deposition temperature for 30 min in order to provide sufficient time and temperature for recrystallization. This resulted in formation of well adherent, black coloured and uniform NiO thin films. The NiO formulation can be represented as:

$$Ni(NO_3) + H_2O \xrightarrow{HCl} NiO\downarrow + HCl\uparrow + NO_2\uparrow \ldots \quad (1)$$

The schematic experimental set up of spray pyrolysis system which is built in our lab is shown in (figure 1). It consists of spray gun with nozzle, substrate heater, automatic temperature control unit, air compressor , pressure regulator, thermocouple, stepper motor with controller and power supply .

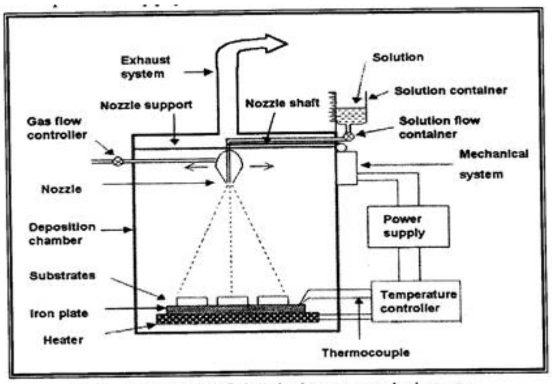

Fig 1. equipments of chemical spray pyrolysis system

3. Results and Discussions

3.1 Structural and Optical properties

The crystalline structure of thin films, obtained at different thickness. XRD instrument is from type (Shimadzu 6000) made in Japan, with the following specifications are target is $Cu_{K\alpha}$ radiation with wavelength, λ=1.54056A°. Generally speaking, the XRD spectrum, the Full-width at the half maximum (FWHM) of the diffraction peak is smaller, the grain size of thin film was larger and the quality of the film was better. This value was smaller than. It proved that the crystalline quality of NiO thin film obtained in experiment was better.

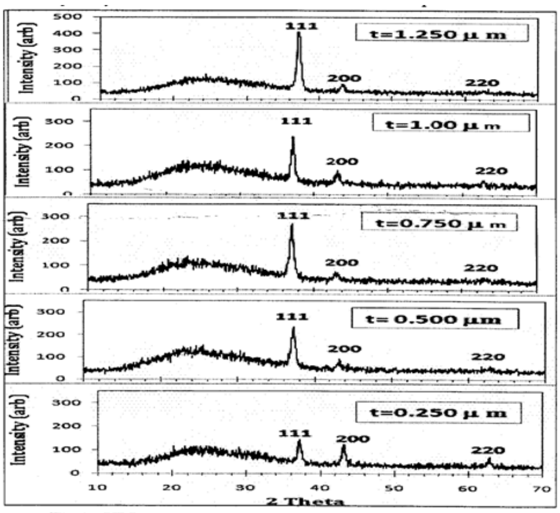

Fig 2. XRD pattern of NiO thin films for different thickness.

The average grain size of nickel oxide thin film samples were calculated by using the Scherrer's equation [14], and there values as table (1)

$$D_{ave.} = \frac{0.9}{FWHM \quad cos\theta_B} \quad \text{.........} \quad (2)$$

Where $D_{ave.}$:is the average grain size.

λ= 1.54056 A° (X-ray wavelength)

θ_B= the diffraction peak position, it means Bragg's angle.

Nickel oxide is a cubic structure. The lattice parameter 'a' can be evaluated from the relation [9] :

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \quad \text{.........} (3)$$

Figure 2 presents the XRD diffraction patterns of the samples prepared at different thickness was obvious as NiO films prepared at 350 ^{o}C substrate temperature. The variation of crystalline grain size increased from 2.67 to 2.78 A^{o} with increasing thickness.

Table 1: Varied XRD parameter of NiO thin films with thickness increasing.

Thickness t (mm)	d_{111} A^{o}	d_{200} A^{o}	d_{220} A^{o}	FWHM for d_{111} (degree)	a A^{o}	$D_{ave.}$ A^{o}
0.250	2.41136	2.0877	1.4792	0.5326	4.17659	2.667702
0.500	2.42819	2.1002	1.48102	0.5100	4.17424	2.89838
0.750	2.41135	2.0902	1.47719	0.7036	4.17658	2.10906
1.000	2.41270	2.0868	1.47482	0.7105	4.17892	2.093778
1.250	2.41512	2.0913	1.47860	0.5144	4.18311	2.782045

3.2 Optical Properties

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.

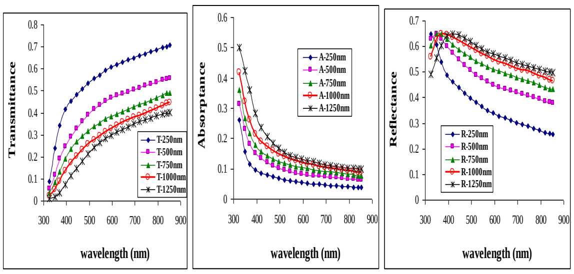

Figure 3: Transmittance, absorptance and reflectance of NiO thin films.

The spectral transmittance and total reflectance of the films were measured by (UV-1650PC Shimadzu software 1700 1650, UV-Visible recording Spectrophotometer), (Phillips), Japanese company UV/VIS/NIR spectrophotometer in the range (190-1100) nm.

Nickel oxide (NiO) thin films were successfully deposited on glass substrate using chemical spray deposition technique. The films are very transparent, firmly adhered to the substrates. The films deposited are 0.25-1.25

μm. Figure 3 shows plots of transmittance, absorbance and reflectance as a function of wavelength. The graphs show that the properties of the films become more defined with increase in thickness. Generally, the films show low degree of transmittance and reflectance, but high degree of absorbance in spectral regions.

From figure 3, it can be seen that all NiO films deposited at different thickness having a high transparency in visible region, while the transparency in UV region was very low. Furthermore, it also can be seen that the optical transparency is reduced with increasing of the increasing of thickness. The transmission spectra of NiO films prepared at 400 ^oC for different thickness is displayed in figure 3 , from transmission spectra observed that the film samples absorb heavily within UV-VIS region but moderately in NIR region for films deposited at room temperature (27 ^oC). The maximum absorbance for films occurred within UV region from where the absorbance decreased with the wavelength towards the NIR region. The transmission has greater than 69% in the VIS-NIR region (at thickness 0.25μm). The properties of poor transmittance in the UV-VIS but moderately high transmittance in the VIS-NIR exhibited by film sample 400 ^oC make the film good material for screening off UV portion of electromagnetic spectrum which is dangerous to human health and as well harmful to domestic animals.

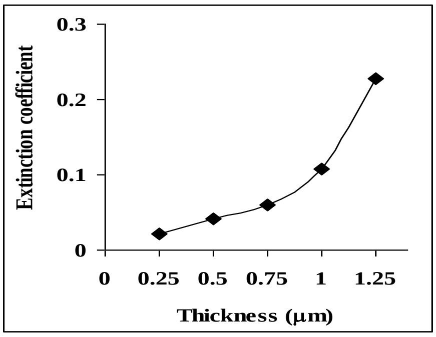

Figure 4: Extinction Coefficient of NiO films as function of thickness.

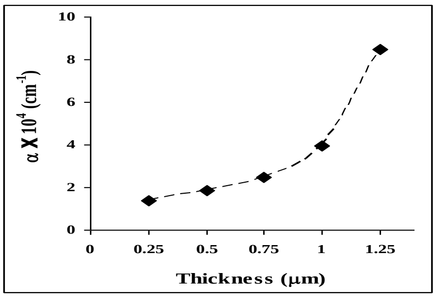

Figure 5: Absorption Coefficient of NiO films vs. thickness various.

In order to determine the optical band gap of the semiconductor, the following dependence of the absorption coefficient 'a' on the photon energy equation [8,14,15] is used, for direct transitions :

$$\alpha\ h\upsilon = A\ (\alpha\ h\upsilon\ - Eg)^{r} \quad \ldots\ldots \quad (4)$$

Where **υ:** is the frequency of the incident photon.

h : is Planck's constant.

A is constant.

E_g: is optical energy gap.

r: is the number which characterizes the optical processes.

r has the value $\frac{1}{2}$ for direct allowed transition, $\frac{3}{2}$ for forbidden direct allowed transition.

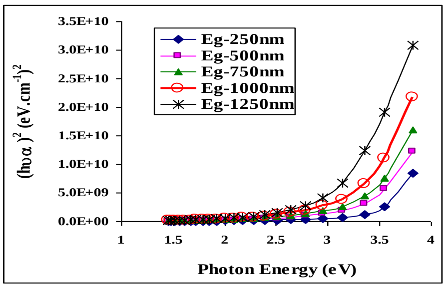

Figure 6: Allowed direct transitions of NiO with thickness various.

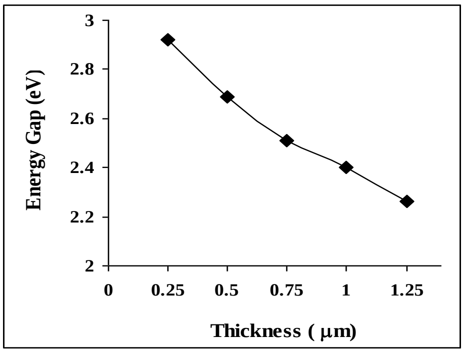

Figure 7: Optical band gap of NiO films as function thickness various.

Table 2: Some optical properties of NiO thin films

Thickness t (mm)	*T*	*A*	*R*	*α X10^4 cm^{-1}*	*n*	*k*	*E_g eV*
0.25	*0.69*	*0.10*	*0.21*	*1.399*	*3.951*	*0.021*	*2.92*
0.50	*0.64*	*0.16*	*0.20*	*1.845*	*3.703*	*0.042*	*2.69*
0.75	*0.57*	*0.22*	*0.18*	*2.464*	*3.469*	*0.060*	*2.51*
1.00	*0.51*	*0.25*	*0.16*	*3.932*	*3.291*	*0.108*	*2.40*
1.25	*0.42*	*0.28*	*0.13*	*8.483*	*3.165*	*0.227*	*2.26*

The outstanding properties of the oxide films show them as good applications electrochromic materials in general. Electrical light modulation devices, such as: non-emissive large scale displays, electrically controlled optical shutters for heat and light modulators for windows, where the switching speed is not a key factor, smart windows (photovoltaic powered electrochromic devices), etc.

4. CONCLUSION

The homemade chemical spray pyrolysis unit has been used to prepare NiO thin films. The dependences of structural and optical properties were investigated of NiO thin films on increase thickness varied from 0.25 to 1.25 mm . The XRD results showed peaks corresponding to the pure nickel oxide films were observed, indicating that no shift in the peak positions. The transmittance and reflectance are generally low with increase thickness in VIS-NIR region , this behavior converse with absorbance which was increased. Allowed direct energy band gap transitions were the most probable transition, and were found to vary from (2.26-2.92)eV for (0.25-1.25)μm respectively of were obtained for the oxide film under various thickness. Values of the refractive index within range (3.95-3.16)

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