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Study of Optical and Electrical Properties of NiO Nanostructure Thin Film

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***Abstract*:- Nickel oxide (NiO) thin films were prepared using a simple spray pyrolysis technique from hydrated nickel chloride salt solution ($Nicl_2.6H_2O$) deposited on glass substrates at temperature (450C°) and with different solution concentrations (0.4-0.6-0.8-1 M). Structural and morphological properties of the grown NiO films were studied using X-ray diffraction (XRD) and atomic force microscope. NiO Films with Nano-grain size were obtained. The value of nanoparticle size ranged from 24.68 nm to 34.08nm. Transmittance spectra recorded using the spectrophotometer in the range of (330-2200 nm). The absorption coefficient and the optical band gab energy were calculated. The band gap of NiO film decreases from 3.7 to 3.2 eV as the molarity increased from 0.6 to 0.1 M. Both the electrical resistivity and the activation energy of the prepared films were calculated.**

Keywords: Nickel oxide - Optical band gab- Spray pyrolysis- AFM.

1- INTRODUCTION:

Nickel oxide thin films are very important to be used in many scientific and technological applications. they have achieved great success when they were deposited on glass substrates in various physical and chemical ways .the most important ways are: Thermal spray, pulsed laser, chemical bath deposition [16].Nickel oxide films have some electrical and optical properties such as band gab in the range of 3.1eV to 4 eV and electrical resistivity is in the range of $10-10^{6}\Omega$.cm [15,12].Nickel oxide (NiO) material has structure like NaCl-type with lattice parameter 4.177 Å [4]. It offers promising candidature for many applications such as solar thermal absorber catalyst for O_2 evolution, photo electrolysis and electrochromic device. Nickel oxide is also a well-studied material as the positive electrode in batteries [3]. In this paper we prepared thin films by the spray pyrolysis (SP) process owing to its several advantages such as low cost of the apparatus ,large area with high homogeneity and easy control of structure of the deposited films.[5]

2- EXPERIMENTAL.

Nickel oxide thin films were deposited from aqueous solution of ($Nicl_2.6H_2O$) by **SPT** on glass substrates. Precursor solution was ($Nicl_2.6H_2O$) of concentration 0.6M, 0.8M and 1 M. This was mixed and stirred in 50 ML distilled water for 10 min. The substrates have been chemically cleaned by standard methods. Nickel chloride solution was sprayed onto the preheated glass substrates, which undergoes evaporation, solute precipitation and pyrolytic decomposition, thereby resulting in nickel oxide thin films according to the following reaction:[13]

$$\boldsymbol{Nicl_2 6H_2O \rightarrow 2Hcl + NiO + 5H_2O} \qquad (1)$$

The thickness of NiO thin Films was measured using weight method, which depends on the difference between weight of substrate before and after deposition of the films. The thickness can be calculated from the relation below: [7, 2]

$$\boldsymbol{t = \frac{\Delta m}{\rho A}} \qquad (2)$$

(**t**): the thickness of the film, ($\boldsymbol{\Delta m}$): the difference between weight of substrate before and after deposition of the Films, (**A**): the area of thin Film and $\boldsymbol{(\rho)}$ is the density of element.

3- RESULTS AND DISCUSSION

3-1 Structural Properties

[**Figures 1**] displays the XRD spectra of the films deposited at different molarities at substrate temperature (450C°)

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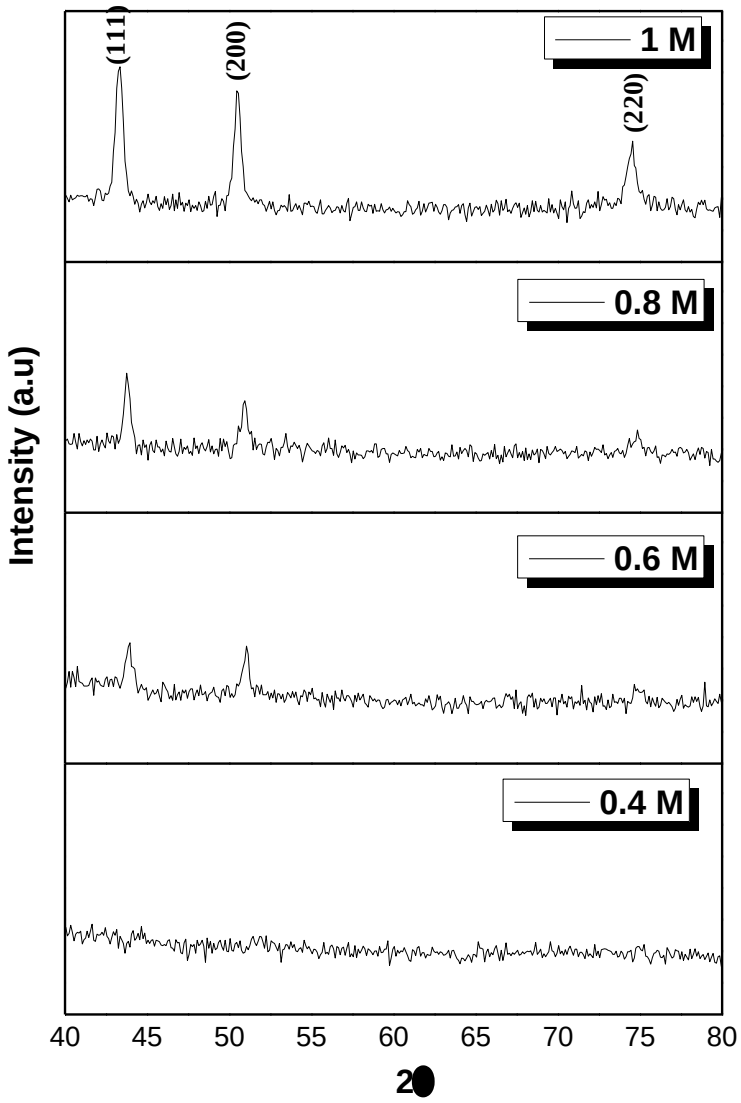

Fig. 1 XRD spectrum for the NiO films deposited on glass and prepared at 450C^{0}of molar concentration (0.4-0.6-0.8-1 M).

The **XRD** spectrum showed that at a molar concentration of **0.4**the film did not crystallize and with increasing of precursor concentration from 0.6 to 1M the commencement of crystallization was observed. It is seen from XRD patterns that three peak appears were given in table (1) which is attributed to the(111), (200) ,(220) diffraction peaks and clearly indicated that the NiO phase exists under its face centered cubic (FCC) structure, which is in good agreement with Joint Committee on Powder Diffraction Standards (JCPDS card number 04-0836).[8,12]

The lattice constant $\boldsymbol{a}$ for **NiO** $\boldsymbol{a}$ phase is calculated using the following equation:[8]

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

$\boldsymbol{hkl}$ are miller indices and d is the interlinear spacing given by Bragg's law:

$$2d \sin\theta = n\lambda \qquad (4)$$

Where $\boldsymbol{n}$ is the order of diffraction taken equal unity (first order), $\boldsymbol{\lambda}$ is the wavelength of the radiation$\lambda = 1.7889$ Å for CO Kα radiation, and θ is the Bragg diffraction angle of peak in degree.

The average crystallite size was obtained using the Debye-Scherer formula in Equation: [12]

$$D = \frac{K.\lambda}{\beta COS\Theta} \qquad (5)$$

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β is full width at half maximum (FWHM) peak intensity (in Radian), **λ** is wavelength, **θ** represent Bragg's diffraction angle and **k** is 0.89respectively. This agrees with the standard lattice constant of NiO film value of 4.176 Å.[4]

Table(1):Values of Bragg angle2θ , lattice constants a,grainsize G, ,full width at half maximumβ, deduced from the (111),(220),(200) peaks of NiO thin films prepared at 450C°with different of precursor concentration .

Precursor concentration	hkl	2Θ(rad)	β(degre)	β(rad)	*a* (Å)	D (nm)
0.6	111	43.83	0.5	0.008	4.150	22.41
	200	51.04	0.4	0.006	4.152	30.71
	220	74.86	0.6	0.010	4.162	20.95
					a=4.154	D=24.68
0.8	111	43.77	0.5	0.008	4.156	22.42
	200	50.95	0.4	0.006	4.159	30.73
	220	74.87	0.4	0.006	4.164	34.90
					a= 4.161	D=29.35
1	111	43.33	0.4	0.006	4.196	29.82
	200	50.48	0.4	0.006	4.196	30.64
	220	74.52	0.3	0.005	4.178	41.78
					a= 4.190	D=34.08

The surface morphology of NiO by(0.6-0.8-1M) was observed with AFM micrographs as shown in Fig.2.

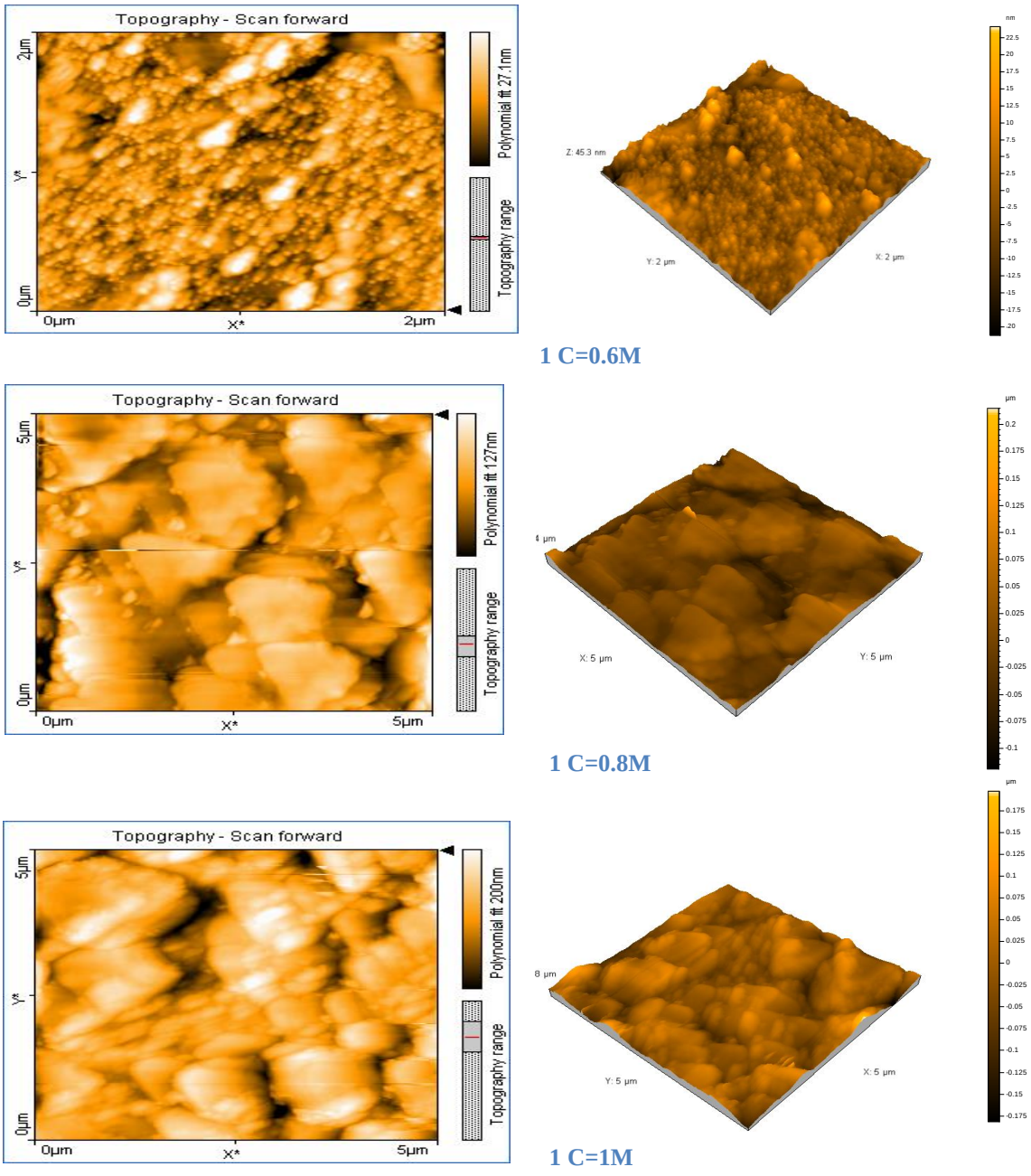

Fig. 2: AFM images for NiO films deposited on glass and prepared at 450C^{0}of molar concentration (0.6-0.8-1 M) for 2D& 3D.

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Figure (2) shows higher molar concentration has increased the crystallite size and RMS roughness of the film. The increase of the crystallite size may be caused by columnar grain growth in the structure. [9,4]

The results of crystallite size obtain from AFM investigation are in good agreement with those obtained from XRD measurements shown in **Table 1**.

AFM results showed homogenous and smooth NiO films. The average of roughness and root mean square (RMS) roughness for NiO, estimated from **AFM**, are given in **Table 2**

Precursor concentration M	Roughness average Sa(nm)	Root mean square Sq(nm)
0.6	13.22	18.23
0.8	17.79	22.33
1	26.6	33.28

3-2 Optical Properties

Transmittance spectra recorded using the spectrophotometer in the range of (330-2200 nm).

Figure (3) shows the transmission spectra of NiO films deposited at different molarities (0.6-0.8-1M).

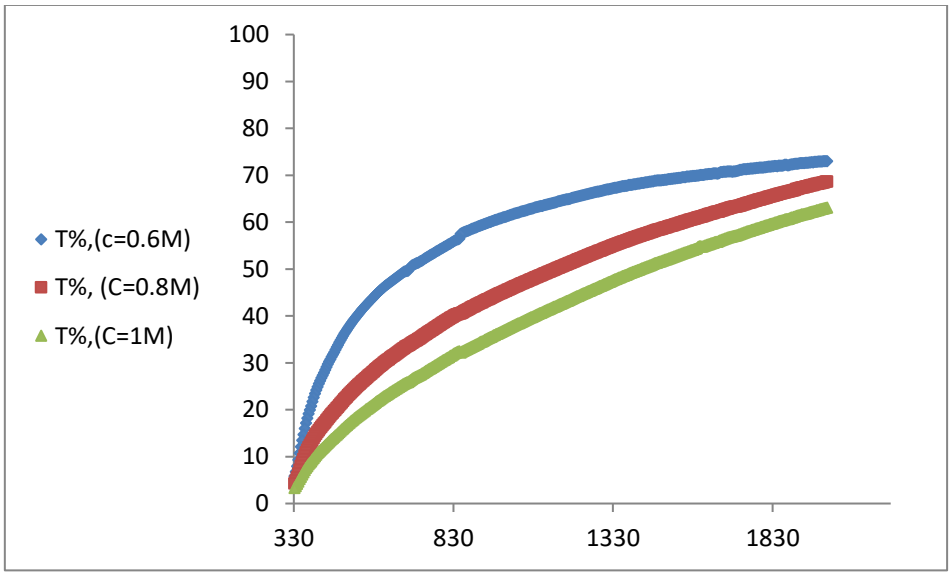

Figure 3: Transmission spectra of NiO thin films.

Figure (3) shows that transmittance decreased from 80 % to 61 % as precursor solution concentration increases (0.6 M to 1 M). This may be ascribed to the increased value of NiO thickness and absorbance [10].

Absorption coefficient, α was obtained using Equation:[2]

$$\alpha = 2.303\frac{A}{d} \qquad (6)$$

(**d**) is the film thickness **&** (**A**) is absorbance.

A plot of Absorption coefficient, **α** against wave length is shown in Fig. 4

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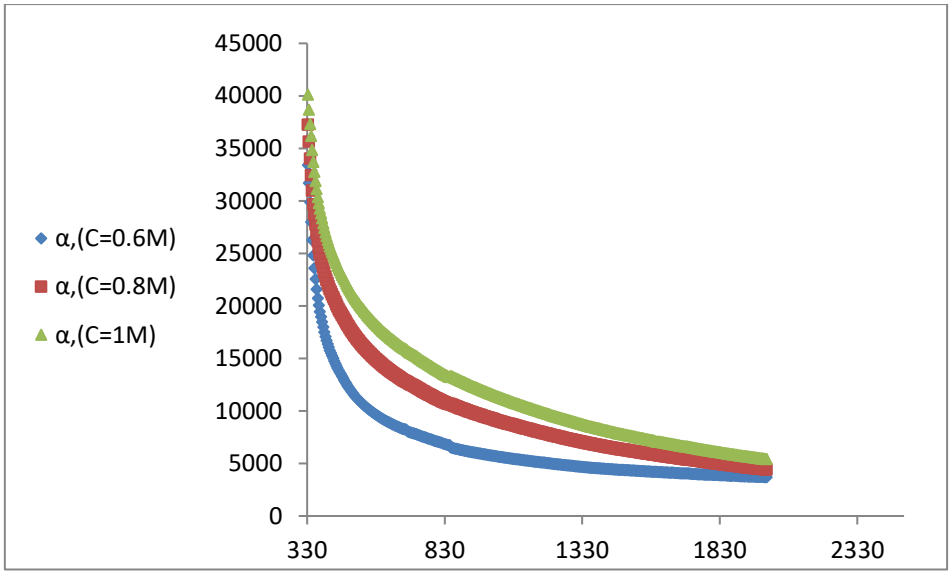


Figure 4. Plot of Absorption coefficient against wavelength of varied NiO film molarity.

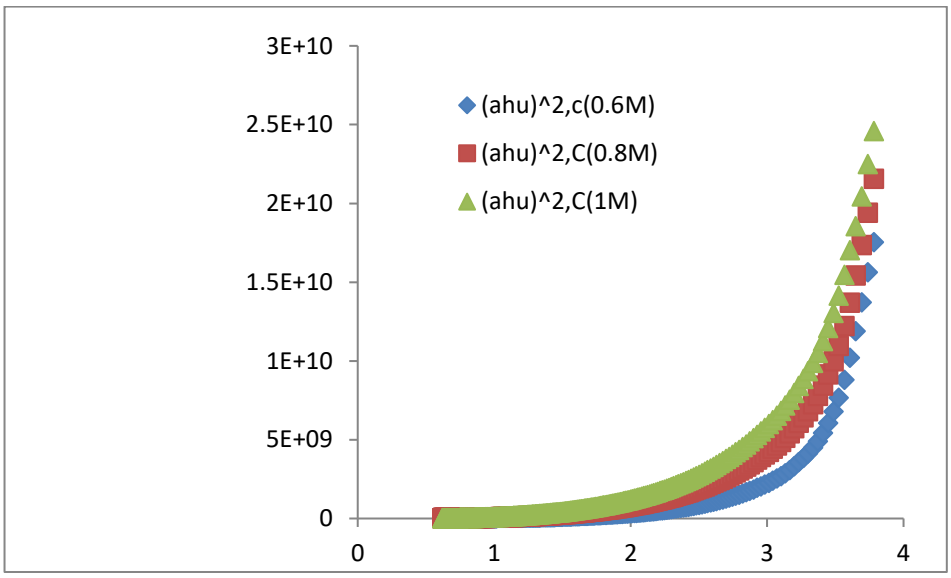
Figure (4) shows that absorption coefficient has decreased by increases wavelength.[5]

Recorded optical data were further analyzed to calculate the band-gap energy of the NiO films using classical relation: [10]

$$\alpha = A\frac{(h\upsilon - E_g)^n}{h\upsilon} \qquad (6)$$

(**n**) is an integer depending on the nature of electronic transitions. For the direct allowed transitions **n** has a value of 1/2 and **A** is energy dependent constant. (**h**) is plank's constant and $\boldsymbol{h\upsilon}$ is the energy of the incident photon, υ is the frequency.

Fig. 5 shows the plot of $(\alpha h\upsilon)^2$ versus hυ for NiO films with different molarity.. The optical band-gap is obtained by extrapolating the straight-line portion of the plot at α= 0.



A decrease in slope of the plot is also observed as precursor concentration increases. A shift towards lower energy is observed according to the value of the optical band gap. The value of band-gap energy changes from 3.7 to 3.2 eV with increase in the film molarity from 0.6 to 1M .This reduction is attributed to the Moss-Burstein shift .[17,2]

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3-3) Electrical Properties

We were studied the variation of electrical resistivity with temperature for NiO films with different molar concentrations (0.6,0.8,1M).

C(M)	$\rho * 10^4 \Omega . cm$
0.6	0.14
0.8	0.2
1	0.26

For all the samples, it is observed that electrical resistivity decreases with an increasing in temperature and supports the semiconducting nature of NiO films and increases with increase in molar concentrations. [12,1]

The thermal activation energies (Ea) is calculated from the local gradients of the lnR VS 1/T plots based on the following Arrhenius equation: [1-18]

$$R = R_0 e^{\frac{-Ea}{kt}} \quad (6)$$

$\boldsymbol{R_0}$ is a constant ,**Ea** is an activation energy and $\boldsymbol{k_B}$ =Boltzmann constant

Figure (6) shows the Plot of lnR against 1/T of varied NiO film molarity

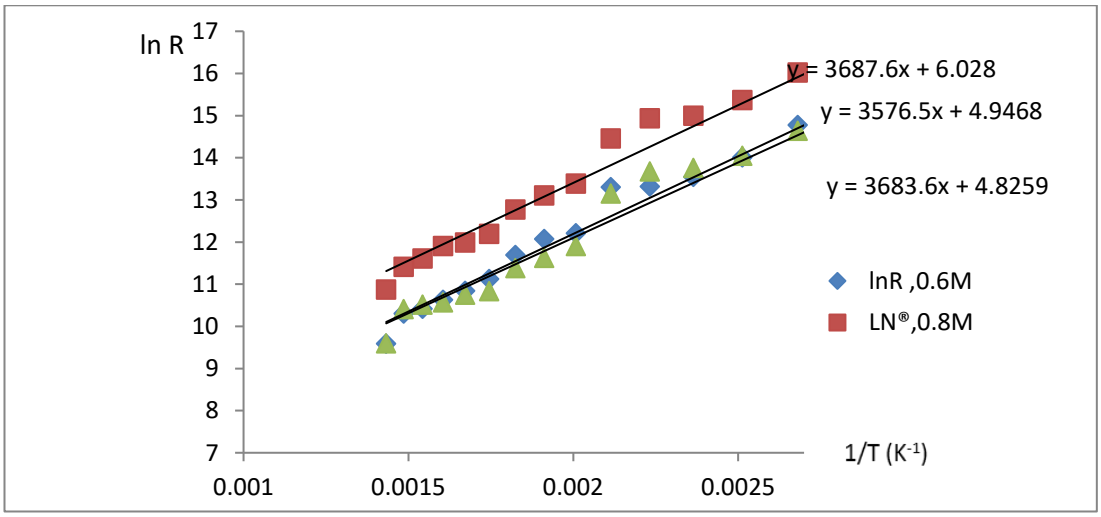

Fig6. Plot of lnR against 1/T of varied NiO film molarity.

The activation energy for NiO samples of different molar concentrations (0.6,0.8,1M) were equal to $Ea = 0.317, 0.318, 0.30$. [10]

4- CONCLUSION:

The **XRD** results reveal that Nickel oxide films with Nano-grain size were obtained with different molar concentrations and were found to be polycrystalline. The XRD data show the dominating peak is (111) and the Nickel oxide films have cubic structure. The **AFM** results reveal that the surface of films is highly smooth. The transmittance value NiO film decreases from 80 % to 61 % as precursor solution concentration increases from0.6 M to 1 M. The optical energy gap of NiO with concentration (0.6,0.8,1M) were equal to3.7,3.5 and 3.2eV. The activation energy for NiO samples of different molar concentrations were equal to $Ea = 0.317, 0.318, 0.30$ eV respectively and electrical resistivity decreases with increasing in temperature.

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