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Fabrication and Characterization of NiO:Al Thin Films

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Abstract: Pure Nickel Oxide (NiO) and thin films (NiO:Al) were prepared using a simple spray pyrolysis technique from hydrated Nickel Chloride salt solution ($NiCl_2$, $6H_2O$). The optical, structural and morphological properties of the fabricated films have been investigated. X-ray diffraction studies revealed a polycrystalline nickel oxide phase with cubic crystalline structure, predominantly with 111, 200 and 222 oriented films. The highest measured optical transmittance in the visible range is 79%. The morphology of the surface samples of thin films were investigated by Atomic Force Microscopic (AFM).

Key words: Optical properties, structural properties, NiO thin films, doping, transmittance, samples

INTRODUCTION

Nickel Oxide thin film (NiO) is an attractive material due to its excellent chemical stability as well as optical, electrical and magnetic properties. It is a group 8-6 semiconductor which has the polycrystalline of cubic structure (Jandow, 2015). The interesting in Nickel Oxide (NiO) thin films is growing fast due to their importance in many applications in science and technology (Romero *et al*., 2010). Nickel Oxide (NiO) has attached considerable attention for applications such as catalysts, electrochromic film, gas sensors, fuel cells and thermoelectric materials (Xiang *et al*., 2010). Nickel oxide p-type conductivity, wide band gap ranging from 3.6-4.0 eV (Fadheela, 2015). The solute must have high solubility to increase the yield of the process, metal chlorides have highest water solubility relative to other metal salts and are used for the industrial production of several oxides and ferrites (Ismail *et al*., 2013). Several methods can be used to prepare NiO thin film such as sol-gel, spray pyrolysis, plasma enhanced chemical vapor deposition, pulsed laser deposition and magnetron sputtering (Fujii *et al*., 1996). Among various methods, spray pyrolysis is low cost and one through which the films can be coated for large area (Ismail *et al*., 2013). In this research, the effect of Al doping on the structural and optical properties of Nickel oxide thin films were studied.

MATERIALS AND METHODS

Experimental: Nickel oxide thin films have been deposited from 0.1 M aqueous solution of Nickel Chloride $NiCl_2{\cdot}6H_2O$ by spray pyrolysis technique onto glass substrate. For Aluminum doping $AlCl_2{\cdot}H_2O$ powder was dissolved in precursor solution of $NiCl_2$ with different Weight percentages (wt.%). The Al-doped films were prepared with various ratio of 0, 0.5, 1, 1.5 and 2 wt.% aluminum concentrations. The NiO films were deposited with the same conditions of: solution volume 100 mL, nozzle to substrate distance 25 cm and the optimized substrate temperature of 350°C. Then, the resulting solution was sprayed on preheated glass substrates to 350°C by an electrical heater when the solution is sprayed the following reaction takes place at the surface of the heated substrate. The deposition parameters applied for the preparation of nickel oxide thin films are presented in Table 1. For Aluminum doping ($AlCl_2$) was dissolved in precursor solution of ($NiCl_2$) with different weight percentage and sprayed onto preheated glass substrate. The NiO doped films were prepared for 0, 0.5, 1, 1.5 and 2% of aluminum concentrations with the same deposition temperature and spray rat.

Table 1: Deposition parameters applied in this research

Parameters	Values
$NiCl_2{\cdot}6H_2O$ solution concentration	0.1 M
Gas pressure	1 bar
Substrate temperature (°C)	350°C
Nozzle to substrate distance	25 cm
Solvent	Distilled water
Deposition time (min)	15 min
Rat of spray	2.5 mL/min
Spray time during each cycle	7 sec

Basic theory: In the present research, the optical properties of NiO:Al thin films were studied as the absorption coefficient (α) extinction coefficient (k_o) and refractive index (N_o). Equation 1 is based on the Beer-Lambert law for optical absorption where, I_o and I are the intensity of incident and transmitted light of the film

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with thickness (t), Absorbance (A) and the absorption coefficient (α) which shown in the following equation (Jafar *et al.*, 2013):

$$\alpha = \frac{1}{t} * \ln\left(\frac{I_0}{I}\right) = 2.303 * \frac{A}{t} \quad (1)$$

The optical band gap of electronic direct transition for the thin films of samples were calculated from the Eq. 2 (Jafar *et al.*, 2013):

$$hv * \alpha = B * \left[hv - E_g\right]^{1/2} \quad (2)$$

Where:
h = The planck constant
v = The light frequency
E_g = The optical Energy gap
B = Empirical constant

The correlation between the Absorption coefficient and the extinction coefficient (k_o) was shown in the following Eq. 3 (Jafar *et al.*, 2013):

$$K_o = \alpha * \frac{\lambda}{4\pi} \quad (3)$$

Where:
λ = The wave length of the incident light
K_o = The correlation between the extinction coefficient
(N_o) = The Refractive Index was given in the Eq. 4 (Fadheela, 2015):

$$N_o = \left(\frac{1+R}{1-R}\right) + \sqrt{\frac{4R}{(1-R)^2} - K_o^2} \quad (4)$$

where, R is the reflectance of the NiO:Al films. From the Debye-Scherrer Eq. 1, the grain size of the crystallite thin film from the XRD data was calculated in the following Eq. 5 (Mikrajuddin and Khairurrijal, 2008):

$$D = \frac{0.9 * \lambda}{\beta * \cos(\vartheta)} \quad (5)$$

Where:
D = The grain size of the crystallite
λ = 1.54059 Å = The wavelength of the X-rays used
β = The broadening of diffraction line measured at the half of its maximum intensity in radians
θ = Angle of diffraction (Mikrajuddin and Khairurrijal, 2008)

RESULTS AND DISCUSSION

Structural properties: The crystallographic structure of NiO:Al films were characterized by X-Ray Diffraction (XRD, Shimadza-6000) using Cu K_α radiation. And was presented in Fig. 1. The XRD analysis indicate that all samples of the films NiO:Al deposited of pure and doping x = 0.5, 1, 1.5 and 2% were polycrystalline and retain the NiO peaks of the film corresponding to 111, 200 and 222 reflections positions, the film deposited with x = 1.5% was disappeared polycrystalline at reflections positions corresponding to 222 as shown in Fig. 2. All the grown films at 350°C are crystalline in nature and all the diffracted peaks observed in XRD spectra belong to the cubic NiO phase, maximum peak along 2θ = 37.15° corresponding with 111 plan. The value of lattice constant for 111 plane was estimated to be 0.417 nm which is very close to that for bulk NiO taken from JCPDS file #04-0835. The intensity of the 111 plane decreases as the doping ratio increases from x = 0.5-2% as shown in Fig. 1. The sizes of the crystallites of pure NiO and NiO:Al samples with 110, 200 and 211 reflections positions were estimated 13.8-33 nm from the XRD results using Scherrer's formula in the Eq. 5 and depicted in Fig. 2. Maximum grain size of polycrystalline was estimated 33 nm along 200 plan to the sample with doping ratio x = 0.05% as shown in Fig. 2.

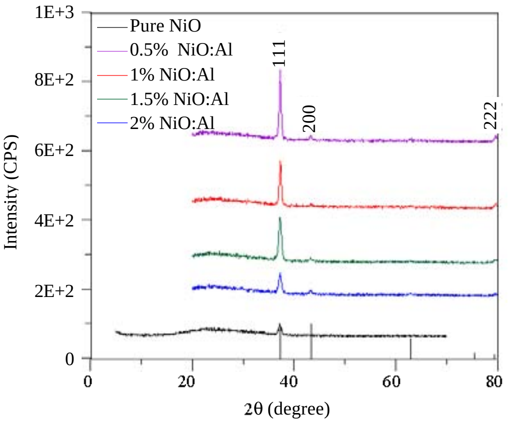

Fig. 1: Depicts XRD analysis of pure NiO and NiO:Al samples

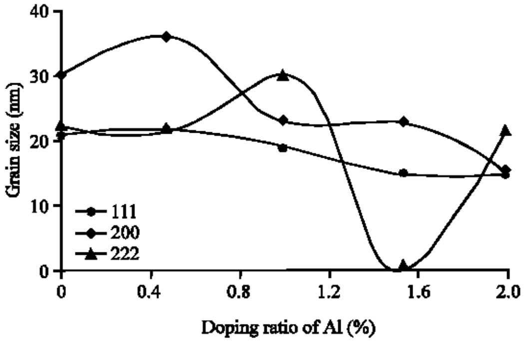

Fig. 2: Inset illustrates the grain size of the doping ratio (x) of NiO:Al

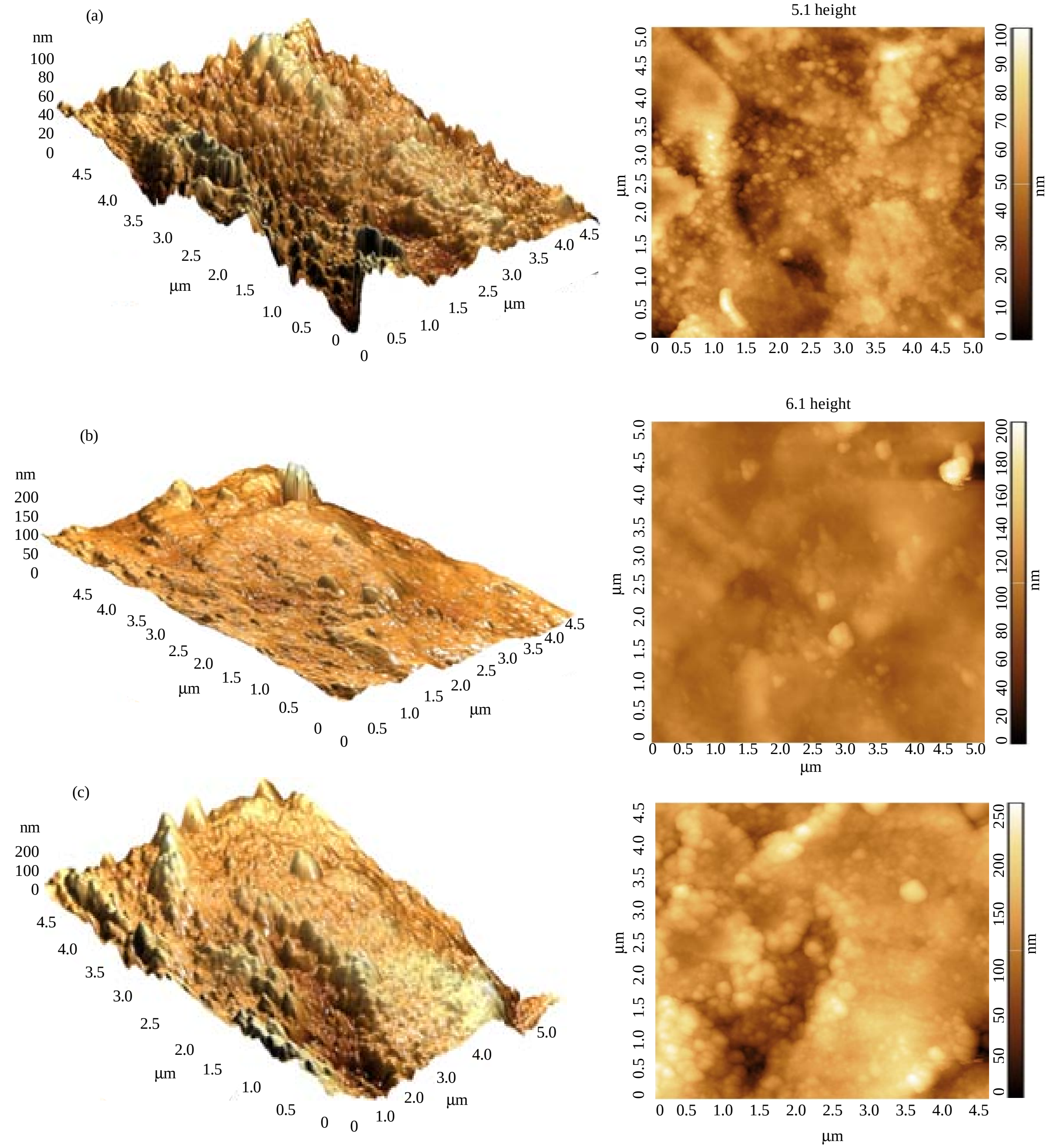

Fig. 3: Depicts 3D and 2D of AFM images of samples doping ratio; a) x = 0.5%; b) x = 1% and c) x = 2%

The morphology of the deposited films were studied using Atomic Force Microscope (AFM) (Angstrom AA3000). Typical 3 and 2D of AFM images of the NiO:Al films synthesized at different doping concentrations x = 0.5, 1 and 2% are shown in Fig. 3.

AFM results showed homogenous and smooth NiO:Al films. The average crystallite size, average roughness and Root Mean Square (RMS) roughness for NiO:Al films, estimated from AFM are given in Table 1. Higher doping 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. The results of crystalline size obtained from AFM investigation are variant with those obtained from XRD measurements via. the Scherrer equation, may be due to that AFM results were described exterior crystalline surface but the XRD results were described interior crystalline structure as shown in Table 2.

Optical properties: The transmittance of pure samples NiO and doping NiO:Al films, deposited on glass substrates, prepared at various doping ratio is presented in Fig. 4. All films synthesized at different doping ratio displayed high transparency in visible and near IR regions with little difference in optical transparency. The optical confinement effect was noticed around 315 nm for pure NiO film prepared as shown in Fig. 4. The $(\alpha*hv)^2$ vs. E plots for the pure NiO and doping NiO:Al films are shown in the inset of Fig. 5. The optical band-gap of the films deduced by extrapolating the linear curve portion to the Energy axis (E) are evaluated 3.478, 3.293, 3.258, 3.223 and 3.183 eV of NiO:Al films deposited with different doped concentrations x = 0, 0.5, 1, 1.5 and 2%, respectively. The optical band gap decreased when the doping ratio increased from 0.5-2% as shown in Fig. 5. This result can be ascribed to the increasing crystallite size with the decrease of doping concentration of the film (Makhlouf *et al*., 2010). The large value of band gap of the pure NiO film is due to quantum size effect (Romero *et al*., 2010).

Table 2: Parameters of the structural properties of NiO:Al samples

Doping concentration (x)	RMS (nm)	Average grain) size (nm) of AFM measurements	Maximum crystalline size (nm) of XRD analysis	Roughness average (nm)
Pure	10.340	34	28	6.430
0.5%	14.525	65	33	11.363
1%	13.892	85	27	9.941
1.5	30.455	110	21	23.436
2%	39.597	75	20	29.821

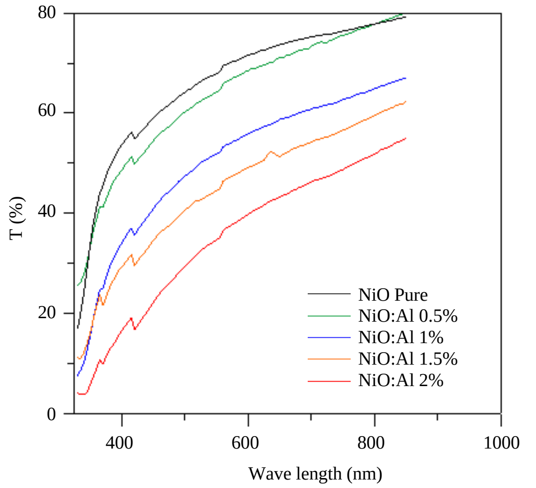

Fig. 4: Transmittance spectra of the NiO:Al films with different doping concentrations

Figure 6a shows the variation of refractive index with photon energy of NiO:Al thin films. The refractive index is shown increased rapidly at the low energies. Then (N_o) decreases at the photon energy which is larger than the energy band gap because of the increasing the direct electronic transitions at that bands energies. The results show that the refractive index values of prepared film have values in the range 1.30-2.5. It can be also said that at every lowest value of refractive index there is highest value for extinction coefficient. Figure 6a is appeared the similar behavior to refractive index (No) for all doping NiO:Al and pure NiO samples. The extinction coefficient is shown in Fig. 6b. From the Fig. 6, it is clear that the extinction coefficient have highest values in the UV region for all doping ratio of NiO:Al and pure NiO films. However, it is almost constant in the visible and NIR range for all films of samples.

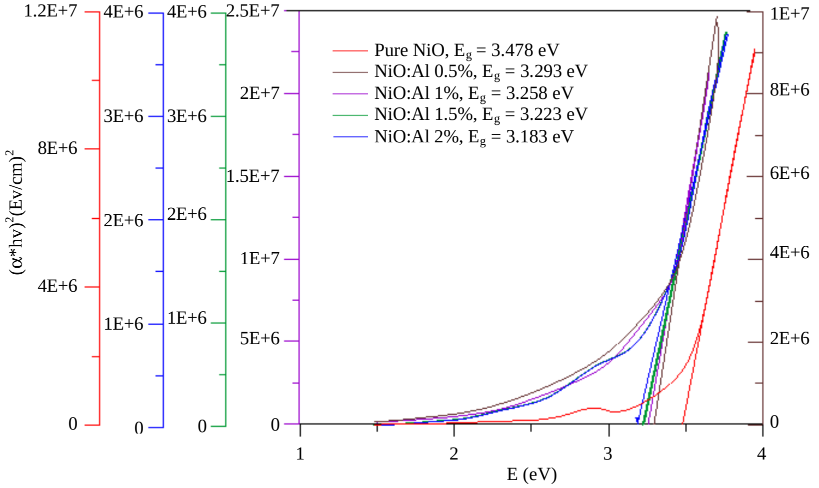

Fig. 5: Optical energy gap of the NiO:Al films with different doping concentrations

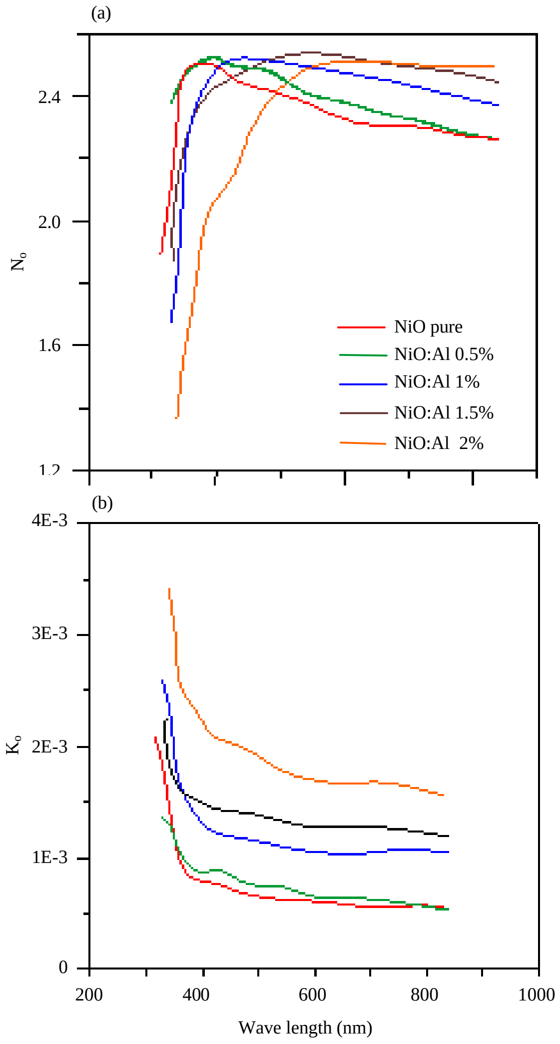

Fig. 6: a) Refractive index and b) Extinction coefficient of the NiO:Al films with different doping concentrations

CONCLUSION

The structural and optical properties of pure NiO and NiO:Al thin films deposited by CVD has been studied. The structural properties showed a good agreement between XRD analysis and AFM to measure a grain size of the films prepared. That clearly, the grain sizes of NiO:Al films increased when the doping ratio of Al increased too. The film exhibits high transmittance for pure samples (~79%) and high absorbance values at ultraviolet region which they decrease rapidly in the visible to the near infrared region. The films were shown a direct transition of energy gap which were evaluated at range 3.18-3.474 eV for allowed energy gap. Refractive index is increased rapidly to high values in the low energy region and remained at constant behavior in the V is region of the all samples NiO:Al films. The extinction coefficients are shown anti behavior of refractive index and increased when increased the doping ratio of NiO:Al.

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