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Structural and Optical Properties of Pure Nio and Li-Doped Nickel Oxide Thin Films by Sol-Gel Spin Coating Method

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Abstract: ***Un-doped and lithium doped nickel oxide (NiO) thin films have been coated on glass substrates by using sol-gel spin coating method. The effect of annealing temperature on the structural and optical properties of NiO thin films were characterized by X-ray diffraction (XRD), Scanning electron microscopy (SEM), UV-visible and photoluminescence spectroscopy (PL) measurements. The XRD result shows the polycrystalline nature of the thin films and the parameters such as grain size (D), dislocation density (δ) and microstrain (ε) were calculated. All the films reveal the most favored orientations along (1 1 1), (2 0 0), and (2 2 0) planes and the structure is confirmed to be cubic. The SEM image displays the surface morphology of Ni and Li-doped nickel oxide thin films. The UV study shows the transmission and absorption spectra and the films have a band gap ranged between 3.53 eV to 3.42 eV. The maximum absorption for the films occurred within the UV region. Transmittance decreases with an increase in the Li concentration. The PL results confirmed that the band gap reduces when the lithium concentration increases.***

Keywords: NiO and Li-doped nickel oxide, Sol-gel, thin films, structural and optical characterization.

1. Introduction

NiO possessing a cubic structure and having density 6.67 g cm^{-3} belongs to an antiferromagnetic material category. The band gap of NaCl-type antiferromagnetic material is in the range of 3.6 – 3.8 eV. NiO has potential applications, such as thermal decomposition of Ni complexes, automobile mirrors, hetero junction solar cells , solar thermal absorber [1], catalyst for oxygen evolution, chemical sensors, electronic devices, energy efficient smart window. Several methods were used for NiO thin film deposition, such as Magnetron sputtering, Rapid thermal oxidation method [2], pulsed laser deposition (PVD) [3], sol-gel method [4]. The sol-gel method is advantageous among these methods because it is simple, inexpensive and composition can be easily controlled. The influence of substrate annealing temperature, number of layer coating and thickness will vary the properties of sol-gel deposited thin films. Stoichiometric NiO have to be produced to improve its application. The reduction in the resistivity of NiO films was noticed by hiking the intentification Ni^{2+} vacancies and doping with monovalent atoms such as Li or Al [5], Electrical properties of Li – doped NiO films [6], improved electrochromic achievement of NiO based thin films by lithium addition: from single layer to devices [7]. The effects of un-doped NiO and Li doped NiO thin films of the structural and optical properties of NiO and Li-doped nickel oxide films were analyzed.

2. Experimental

2.1 Preparation of precursor solution

Nickel chloride hexahydrate ($NiCl_2.6H_2O$) (purchased from Merck), Lithium chloride monohydrate ($LiCl.H_2O$) as dopant and butanol as a solvent are used as source materials for coating Li: NiO and un-doped NiO thin films. The precursor solution was prepared by diffusing 0.4 M nickel chloride hexahydrate in 20 ml of butanol which is used as a solvent. The solution was stirred one hour for blending purposes. Lithium chloride monohydrate of different concentrations (0.14 mole % and 0.21 mole %) is added to the precursor solution. The solution was stirred initially for 1 hour and 10 wt% of citric acid is added to the solution which produce a clear and uniform green colored solution. The final solution was agitated for 24 hours

2.2 Coating of thin films

The prepared solution was used for coating onto a glass substrate. The substrate was spin coated in three steps with speed 3000 rpm, 2000 rpm and 3000 rpm at 30,15,30 seconds respectively. Then the glass substrate was placed on a hot plate at 160^0C for 10 min for dehydrate the films. The substrate was then located in a 400^0C furnace for 30 min to vaporize the solvent and remove the residues. The spin coating procedure was repeated again for 7 times. Finally the glass substrate was placed on the furnace at 450^0C for 1 hour in air to form nickel oxide. The formation mechanism of nickel oxide is

$$NiCl_2.6H_2O \xrightarrow{450^{\circ}C} 2HCL \uparrow + 5\ H_2O \uparrow + NiO$$

HCL and water evaporated in the annealing temperature.

3. Result And Discussion

3.1 Structural analysis

3.1.1 X-ray diffraction

X-ray diffraction analysis was carried out to investigate the structural properties of Pure NiO and Li-doped nickel oxide thin films deposited on the glass substrates. It was preheated at 160^0 C and annealed at a temperature of 450^0 C for 1 hour. The deposited NiO films annealed at 200^0C and it changes to polycrystalline nature only after annealing at 450□C. Therefore the films are thermally annealed at the temperature of 450□C. XRD patterns show that the un-doped and doped NiO thin films annealed at 450^0 C are polycrystalline in nature. The observed 2θ value of the deposited NiO and Li:NiO films were compared with the standard JCPDS card No (75-0197). The favored orientations are (1 1 1), (2 0 0) and (2 2 0) planes and are in good agreement with the standard values. Li doping in NiO thin films suitably modified the crystalline structure of pure NiO. An enhancement in the intensity of the peaks can be attributed either to the grain growth associated with the degree of crystallinity with respect to increase in the solution concentration. The average grain size of the pure NiO and Li:NiO films have been calculated using the formula

$$D = \frac{0.9\lambda}{\beta \cos\theta} \text{ (nm)}$$

where 'β' = full width half maximum of the prominent peak, 'λ' = wavelength of the X-ray diffraction, 'θ' = angle of diffraction and the XRD parameters have been summarized in Table 1. The grain size of the lithium doped thin films has decreased when compared to pure NiO thin film.

Table 1: parameters calculated using X-ray diffraction

Samples	Grain size (nm)	Dislocation density ($x10^{15}$ m^{-2})	Lattice parameter (Å)	Micro strain ($x\ 10^{-3}$)
NiO Pure	22.6	3.9	4.1	1.9
Li:NiO (0.14%)	15.5	4.1	4.1	1.8
Li:NiO (0.21%)	15.9	3.9	4.1	1.8

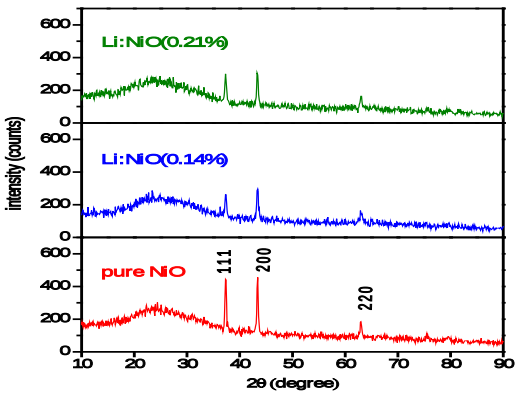

Figure 1: X-ray diffraction patterns of NiO and Li-NiO thin films

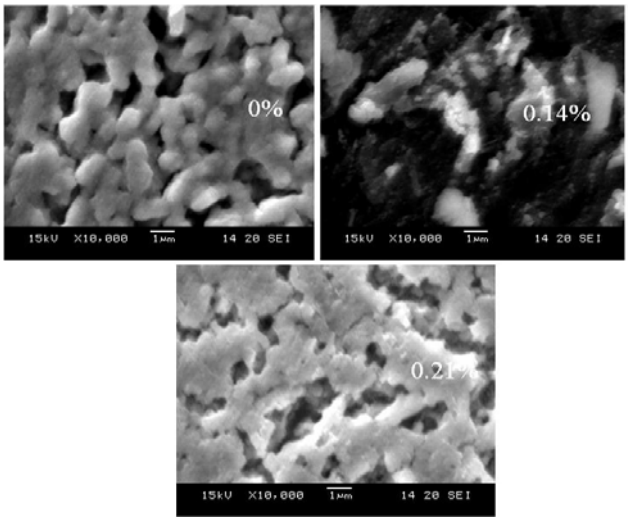

Figure 2: SEM for Pure NiO and Li:NiO thin films.

3.1.2 Surface morphology

Scanning electron microscopic images obtained for the pure and doped NiO films are shown in Fig 2. SEM images show the surface morphology of Ni and Li: NiO thin films. It has circular grains and agglomerated with each other. The crystalline grains are randomly arranged.

3.2 Optical Properties

3.2.1 UV-visible spectroscopy

Fig 3.1 shows that the optical transmittance spectra of the NiO and Li:Nickel oxide thin films. It was analyzed in the range of 300 to 1200 nm. From the transmittance spectra, it was observed that the film sample absorb in the UV region. The highest transmittance value is 79% for 0.14 mole % doped NiO. The optical transmittance data were taken to obtain the optical band gap. The band gap of the films is determined by plotting $(\alpha h\nu)^2$ vs hν. The optical band gap energies for Pure NiO and Li-nickel oxide films were estimated to be 3.62 to 3.54. We concluded that the band gap energy increases compared to that the Pure NiO samples and it varies slightly with the increase of the Li concentration. The absorption co-efficient can be calculated by the following equation. $\alpha = \frac{\ln(1/T)}{t}$

where T = Transmittance and t = thickness of the sample

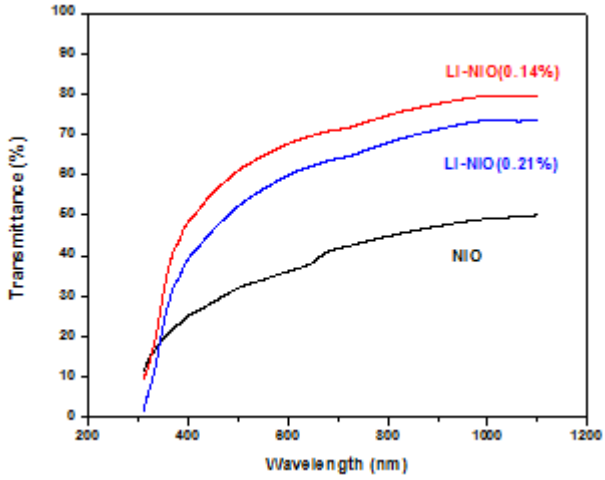

Figure 3.1: Transmittance spectrum of the NiO and Li-NiO.

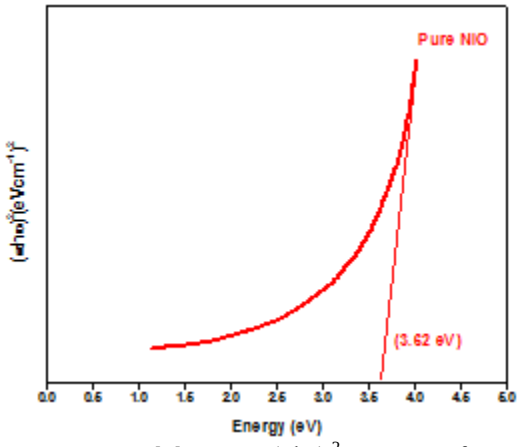

Figure 3.2: Graph between $(\alpha h\nu)^2$ vs Energy for pure NiO

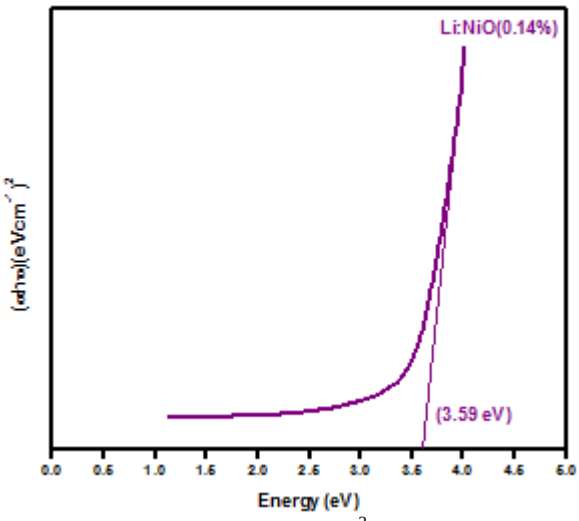

Figure3.4: Graph between $(\alpha h\nu)^2$ vs Energy for 0.21 mole % doped NiO.

3.22 Photoluminescence spectroscopy

The high intense peak corresponds to the NiO. The peak is shifted to the high wavelength (red shift) region upon increase in the dopant concentration in the NiO thin films. Hence the bandgap has been decreased upon increase in dopant concentration.

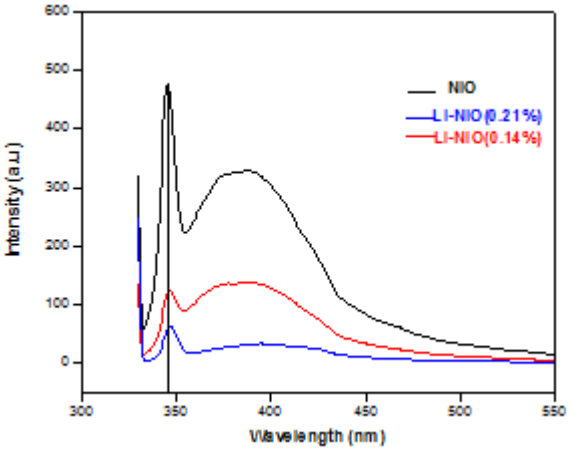

Figure 4: PL spectra of pure NiO and Li:NiO thin films.

4. Conclusion

The deposited undoped and doped NiO thin films annealed at 450°C are found to be polycrystalline in nature. The structure of the NiO is cubic. The average grain size of the nickel oxide is 25nm as revealed from X-ray diffraction calculations. The grain size has decreased by adding the lithium dopant in NiO. The bandgap calculated from the uv-visible absorption spectra confirmed that NiO was a semiconductor material. The transmittance increased by adding the lithium concentration to 0.14 mole%. However further increase in lithium concentration to 0.21 mole% has decreased the transmittance. The band gap was decreased with increase in the lithium concentration. The red shift as evidenced from the PL spectra showed that the band gap is decreasing. The structural and optical properties of the un-doped nickel oxide and lithium doped nickel oxide thin films were studied.

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