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Synthesis and Characterizations of Nanocrystalline Na and Al Codoped Nio Thin Films

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Abstract: In the present work, Na and Al codoped NiO thin films were successfully deposited on a glass substrate by spray pneumatic method. The effect of Al concentration on optical, structural and electrical properties was studied. The transmission spectra show that the Na and Al codoped NiO thin films have good optical transparency in the visible region. The optical band gap energy increased after co-doping by Al to the maximum value of 3.926 eV for 2 % Al. The minimum value of Urbach energy was obtained at a high Al concentration it is 0.319 eV for 3 % Al. The Na and Al codoped NiO films have a minimum electrical resistance was obtained for 1 % Al. XRD patterns of the Na and Al codoped NiO thin films indicating that the structure of Na and Al codoped NiO thin films have a cubic structure of NiO phase.

Keywords: NiO; Thin films, Na, Al cooping, TCO, spray pneumatic method

1. Introduction

Nickel oxide is one of the most important semiconductors materials in the environment field due to the detecting toxic gases [1]. Nickel oxide has several different applications such as sensors, fuel cell electrodes, catalysis, thermoelectric devices, dye-sensitized solar cells (DSSCs) and electrochromic material for displays [2-8]. However, in the latest research to find suitable material with enhanced properties for gas sensing applications, it is centered on the semiconductor nature in optical transparency and electrical conductivity due to the applied interaction. Moreover, several studies have been sensitive to find that the NiO has high optical transparency and good electrical conductivity at various experimental conditions. Among them, NiO thin films with a bandgap of 3.5 to 4.3 eV [9,10].

The purpose of this work is because the material used in the work is rather new. Through research in several areas, we found that three articles touched on codoped NiO thin films. Yan et al [11], studied the structural and magnetic properties of deposited F and Li codoped NiO thin films by pulsed laser technique. Found that adding the Li codoped play an important role in the increases of saturation magnetic moment, which was observed as a newly detected phase in the structural property. This phenomenon showed that the Fe and Li dopants are in corporate substitutionally into the NiO lattice. Chen et al [12]. They studied the effect of Li content on electrical and optical properties of p-type LixCu0.1Ni0.9-xO thin films. Found that the transmittance increased, and the electrical resistivity decreased with increasing the Li content in all films. The optical bandgap energy of about 3.27 eV was obtained for the LixCu0.1Ni0.9-xO thin film. They discussed that the Li, Cu–codoped NiO thin films can be utilized as p-type transparent conducting oxides. Qureshi et al [13]. They studied the preparation and characterization of Li and Ti codoped NiO nanocomposites

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for gas sensors application. XRD showed a single phase NiO at 500 C° and TEM investigation revealed that the particle sizes ranged from 5 to 40 nm, the thin film of LTNO gas sensor showed the highest sensitivity to toluene followed by methanol and chloroform at RT and the maximum sensitivity was obtained for toluene vapor at R.

However, we have studied the Na doped NiO thin films by spray deposition on a glass substrate at 420 °C [14]. These results were published in Materials Research, which was studied the effect of Na doping on optical, structural and electrical properties of Na doped NiO thin films. We found that an only (111) peak was observed for Na doped NiO thin film for monocrystalline NiO with a cubic structure. Na doped NiO thin films have good optical transparency in the visible region and best electrical resistance of 3 at.% Na doping. The surface of thin films can be modified by various techniques such as chemical treatment, thermal treatment, electrochemical treatment and anodisation methods [15].

In this work, we have deposited the Na doped NiO thin films at various Al concentrations to investigate the structural, optical and electrical properties. The thin films were elaborated on a glass substrate at 420 °C by using a spray pneumatic method for 2 ml/min of deposition rate.

2. Experimental Procedure

Na and Al codoped NiO solutions were prepared by dissolving 0.1M nickel chloride hexahydrate ($NiCl_2$, $6H_2O$) and Na/Ni = 2% of sodium chloride dehydrate ($NaCl_2$, $2H_2O$) and x% of aluminum chloride dehydrate ($AlCl_2$, $2H_2O$) with the ratio of Al/Ni = 0, 0.01, 0.02, 0.03 and 0.04. The mixtures solutions were dissolved in the solvent containing equal volumes of absolute ethanol solution (99.995%) purity. The HCl solution was added to stabilize the solution; which was stirred at 50 °C for 120 min to yield a clear and transparent solution. The final solution of NiO was obtained according to the following equations:

$$NiCl_2 + 6H_2O \rightarrow 2HCl + Ni(OH)_2 + + 4H_2O \tag{1}$$

$$NiCl_2 + 6H_2O \rightarrow 2HCl + NiO + 5H_2O \tag{2}$$

Na and Al codoped NiO solutions were deposited on heated glass substrates at 420 °C by spray pneumatic method, which it is transforms the liquid into a stream formed with uniform and fine droplets of 25 µm average diameters.

The optical transmission of deposited thin films was obtained in the range of 300–700 nm by using an ultravioletvisible spectrophotometer (LAMBDA 25). The structural properties of Na and Al codoped NiO thin films were studied by X-ray diffraction (XRD Bruker AXS-8D) with CuKα radiation (λ = 0.15406 nm) in the diffraction angle range (2θ) of 20° and 50°. The electrical resistance R was measured by four-point methods.

3. Results and Discussion

3.1. Optical Characteristics of Na and Al Codoped Nio Thin Films

Fig. 1 shows the variation of optical transmission of Na and Al codoped NiO thin films with various Al concentrations; it is measured with a wavelength in the range of 300 to 700 nm. The Na and Al codoped NiO thin films exhibit a good optical transmission was observed between 45 and 65% in the visible region. However, the Na and Al codoped NiO thin film prepared for 2% Al and 3% Al has high transparency due to the simple corporation between Ni and Al in the substitutional site.

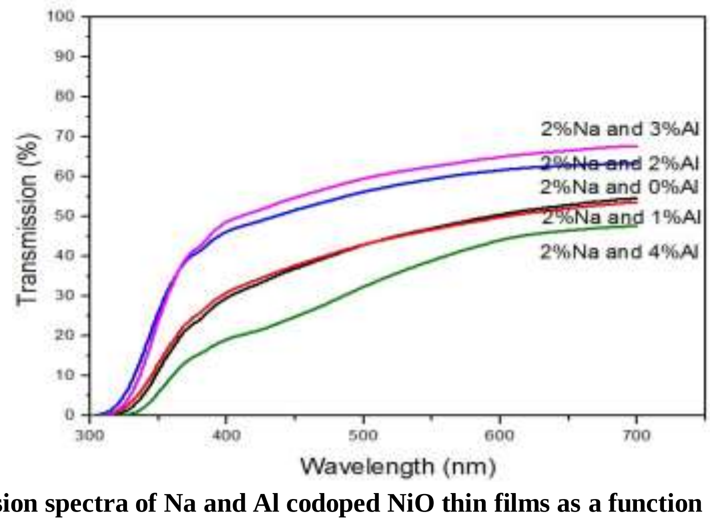

Fig. 1 - Transmission spectra of Na and Al codoped NiO thin films as a function of Al concentration

The optical band gap (Eg) of Na and Al codoped NiO thin films was derived assuming allowed direct transitions between the absorption edge of the valence and conduction band. It is

$$A = \alpha d = -\ln T \tag{3}$$

$$(Ah\upsilon)^2 = B(h\upsilon - E_g) \tag{4}$$

determined by the transmission spectra according to the following equations [16]:

Where A is the absorbance, d is the film thickness; T is the transmission spectra of thin films; □ is the absorption coefficient values; B and C is a constant, h□ is the photon energy and E_g the band gap energy of Na and Al codoped NiO thin films. The optical band gap E_g was obtained by extrapolating the linear portion of the plot

$(Ah□)^2$ versus (h□) to A=0(see Fig. 2).

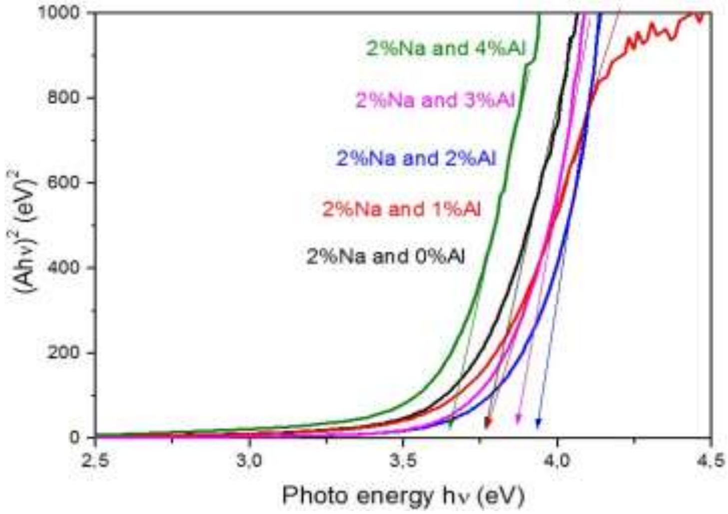

Fig. - 2 Plot of $(Ah□)^2$ versus (hν), to determine the optical band gap in Na and Al codoped NiO thin films with various Al concentrations

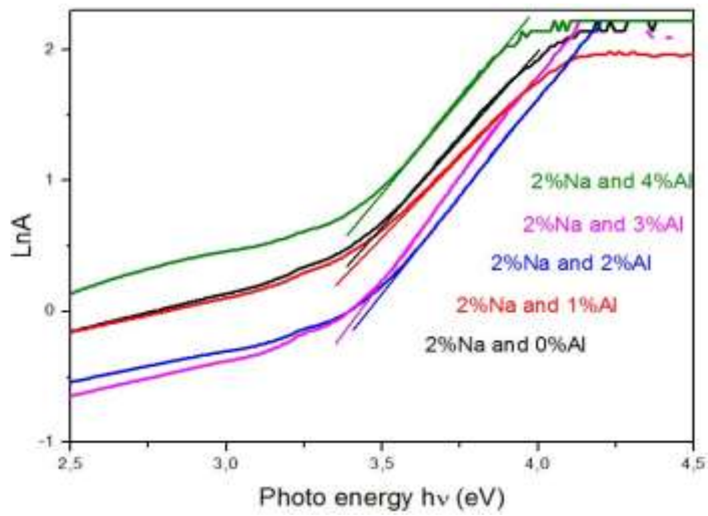

Fig. 3 - The drawn of ln$A$ as a function of photon energy (h□), for deduce the Urbach energy in Na and Al codoped NiO thin films

The Urbach energy (E_u) of Na and Al codoped NiO thin films also can be calculated by the transmission spectra according to the following equations [17]:

$$A = A_0 \exp\left(\frac{h\upsilon}{E_\mu}\right) \quad (5)$$

Where A_0 is a constant and E_u is the Urbach energy, it is also determined by the curves of *LnA* a function of photon energy $h\nu$ as shown in Fig. 3.

The variations of the optical gap energy and Urbach energy of Na and Al codoped NiO thin films as a function of Al concentration are shown in Fig. 4. Firstly, the variation of optical band gap energy is inverse of the variation of Urbach energy of Na and Al codoped NiO thin films. Secondary, the increase in the Urbach energy from 0%Al to 1%Al with stabilizes of the optical gap can be explained by the integration between Na and Al to a p-type semiconductor. The increase in the optical gap energy from 1%Al to 2%Al with decreasing the Urbach energy also can be explained by the Burstein–Moss effect, which are causes the widen energy band (blue-shift). This is the phenomenon that the Fermi level merges into the conduction band with an increase in the carrier concentration. In the end, when the Al concentration increases up to 4%, the optical gap energy was decreased and the Urbach energy decreased due to the oxygen vacancy, the minimum Urbach energy was reached at 3%Al it is 0.319 eV.

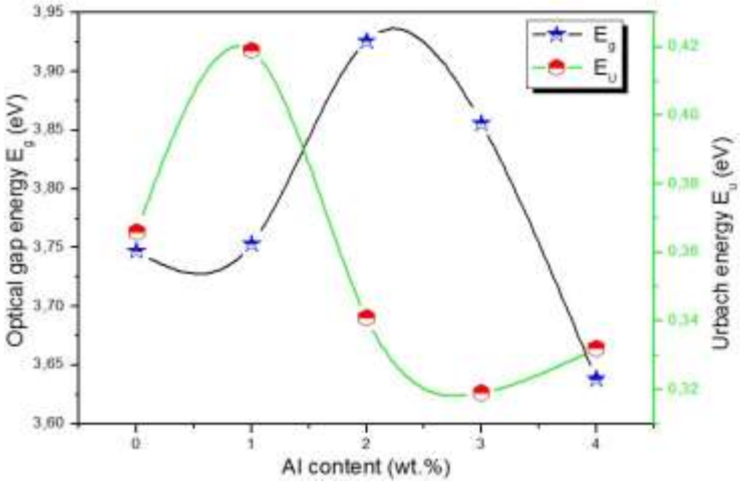

Fig. 4 - The variation of optical gap energy and Urbach energy of Na and Al codoped NiO thin films as a function of Al concentration

The broadening of the optical band gap is an important parameter to advance materials for potential visible light gas sensing applications involving metal oxide nanostructures. The optical gap energy can be correlated with Urbach energy to finding a new linear fitting in all deposited thin films, the proposals model as expressed as (see Fig. 5):

$$E_g = -0.58 E_u + 3.98 \tag{6}$$

Fig. 5 reported the variation of the optical gap energy experimental and linear fitting as a function of Urbach energy. The broadening of the optical band gap of Na and Al codoped NiO thin films due to the narrowing in the conduction band EC and the valence band EV, and causes the motion of EC upwards and EV downwards.

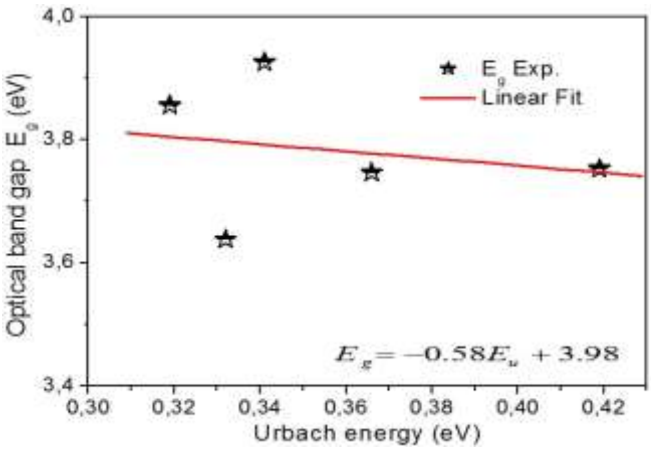

Fig. 5 - The correlation between the optical band gap and Urbach energy of Na and Al codoped NiO thin films

3.2. Electrical properties Na and Al codoped NiO thin films

The electrical resistance of Na and Al codoped NiO thin films was determined by four-point probe method, it is based on measuring the sheet resistance of the films as expressed by:

$$R_{sh} = \frac{\pi}{\ln(2)} \cdot \frac{V}{I} \tag{7}$$

Where I is the applied currant = 1 nA and V is the measurement voltage.

Fig. 6 shows the variation of the electrical resistance of Na and Al codoped NiO thin films as a function of Al concentration. As can see, the electrical resistance decreases after codoping to the minimum value for 1%Al. However, the increase of Al concentration up to 3%, we have obtained an increase in the electrical resistance, when Al concentration increase from 3 to 5%, we have obtained a reduction in electrical resistance. The decrease of the resistance of the Na and Al codoped NiO thin films can be explained by the displacement of the electrons, the latter comes from the Al^{+3} donor ions in the substitutional sites of Ni^{+2}, and formation of the molecular NiNaAlO existed on the surface.

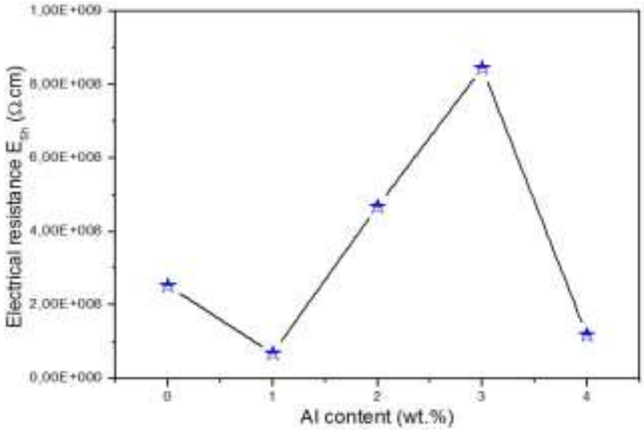

Fig. 6 - The electrical resistance variation of Na and Al codoped NiO thin films as a function of Al concentration

3.3. Structural Properties of Na and Al Codoped Nio Thin Films

The results of the structural characterization of Na and Al codoped NiO thin films are shown in Fig. 7. It can be noticed that all the patterns exhibit diffraction peaks around (2θ~37° and 43°) referred to (111) and (200) crystal plan, respectively [18,19]. The positions of obtaining peaks with and without a presence in the XRD spectra indicating that the Na and Al codoped NiO thin films are nanocrystalline of the cubic structure, which was agreed with other reports [20]. However, the good crystallinity was obtained for Na 2% and Al 1% codoped NiO thin film.

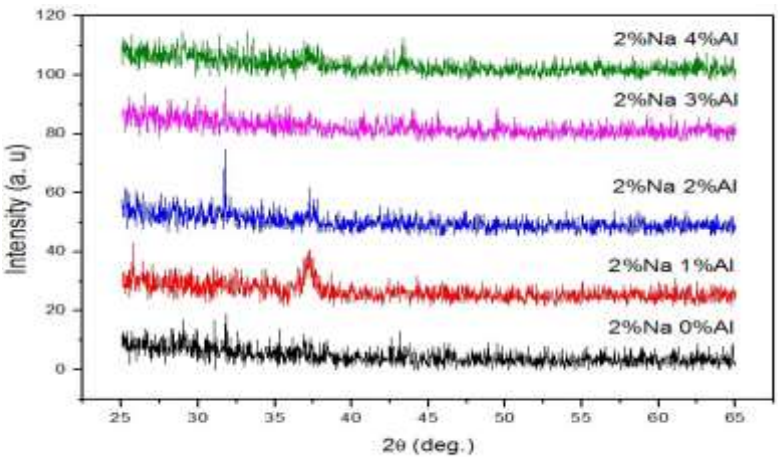

Fig. 7 - X-ray diffraction of Na and Al codoped NiO thin films as a function of Al concentration

4. Conclusion

In conclusion, the Na and Al codoped NiO thin films (Al% = 0, 1, 2, 3 and 4%) were successfully deposited on a glass substrate by spray pneumatic method using nickel chloride hexahydrate, sodium chloride and aluminum chloride dehydrate. The effect of Al co-doping on optical, structural and electrical properties of Na, Al codoped NiO thin films were investigated. The transmission spectra show that the Na and Al codoped NiO thin films have good optical transparency in the visible region. The band gap energy was increased after co-doping by Al to the maximum value was

3.926 eV for 2%Al. The minimum value of Urbach energy is 0.319 eV for 3%Al. The minimum electrical resistance of the Na and Al codoped NiO films was located for 1%Al. XRD patterns of the Na and Al codoped NiO thin films indicate that obtaining thin films is a cubic structure of NiO phase.

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