Original Article

Preparation of Al-doped NiO thin films by spray pyrolysis technique for CO gas sensing

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ABSTRACT

Undoped Nickel oxide (NiO) and Al-doped (NiO:Al) thin films were prepared by spray pyrolysis technique from a hydrated salt solution of nickel chloride (NiCl2.6H2O). The structural, morphological and sensing properties of the prepared films have been studied. X-ray diffraction investigation showed a polycrystalline (NiO) phase with a cubic crystalline structure. The morphology of the surface samples of thin films was investigated by Atomic Force Microscopic (AFM). The sensing properties of prepared nickel oxide thin films showed that the sensitivity to CO gas increased with changing aluminum doping.

Keywords: CO, Sensor, NiO thin films.

Introduction

Nickel oxide (NiO) thin film is a good-looking material because of its admirable chemical stability, optical, electrical and magnetic properties. NiO is (VIII-VI) semiconductor group which has Polycrystalline with cubic structure [1]. The interest in NiO thin films is increasing fast because of their significance in various applications for science and technology [2]. NiO has attached substantial attention for catalysts, electrochromic film [3-5], gas sensors [6], fuel cells [7], anti-ferromagnetic materials [8], anode material in organic light emitting diodes [9] and thermoelectric materials [8]. Nickel oxide is p-type conductivity [10], with the range of band gap between 3.6 to 4.0 eV [11]. Metal chlorides have the highest water solubility comparative to other metal salts. Metal chlorides are used in industrial production of numerous metal oxides and ferrites [12]. Several techniques can be used to prepare NiO thin film such as sol-gel [13], spray pyrolysis, plasma enhanced chemical vapor deposition [14], pulsed laser deposition [15], chemical bath deposition [16] and magnetron sputtering [17]. Spray pyrolysis method is low cost and one through which the films can be coated for the large area [5]. The properties of films that are prepared by spray deposition depend on the substrate, spray rate, substrate temperatures and droplet sizes [18]. Drop size depends on nozzle diameter, spray rate and gas pressure [19].

In this work, the influence of Al doping on structural, optical and sensing properties of NiO thin films are studied.

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Experimental

Nickel oxide thin films were prepared from a 0.1M aqueous solution of $NiCl_2.6H_2O$ using spray pyrolysis technique on a glass substrate. $AlCl_3.H_2O$ material was melted in a precursor solution of $NiCl_2$ for aluminum doping with different weight ratio percentages (wt. %). The Al-doped films were prepared with various ratios of 0, 0.5, 1, 1.5 and 2 wt. %. The NiO films were deposited with the same conditions of solution volume 100 ml; the distance of the nozzle to substrate is 25 cm, and the optimized substrate temperature is 350 °C. The resulting solution was sprayed on preheated substrates. Substrates were heated to 350 °C by using an electrical heater. When the solution was 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 ($AlCl_3$) was dissolved in the precursor solution of ($NiCl_2$) with different weight percentage and sprayed onto preheated glass. The NiO doped films were prepared for 0, 0.5,1, 1.5, and 2 wt.% of aluminum with the same deposition temperature and spray rat.

Table 1: Deposition parameters applied in present work.

NiCl2.6H2O solution concentration	0.1M
Gas pressure	1 bar
Substrate temperature(°C)	350 °C
Nozzle to substrate distance	25 cm
Solvent	Distilled water
Deposition time (minutes)	15 min
Rat of spray	2.5 ml/ min
Spray time during each cycle	7 Sec

Result and Discussion

A. Structural properties: -

The crystallographic structure of NiO:Al films were characterized by XRD, which is presented in Fig (1). The XRD analysis indicates that all samples of the films NiO:Al deposited of undoped and doping (x= 0.5, 1, 1.5 and 2) wt% 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 prepared samples at 350 °C are crystalline, and all the diffracted peaks witnessed in XRD pattern refer to the cubic NiO phase, maximum peak alongside $2\theta=37.15$ corresponding with 111 plan. The value of lattice constant for 111 plane was valued 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 with the increase of doping ratio from x = 0.5 to 2 wt.%, as shown in Fig (1). The crystalline sizes of the crystallites of pure NiO and NiO:Al films with 111, 200, and 222 reflections positions were estimated to be 13.8 to 33 nm from the XRD results using Scherer's formula [20] in Eq (1) and described in Fig (2).

$$D = 0.9\,\lambda / \beta\ \mathrm{COS}\theta \qquad (1)$$

Where D: crystalline size of the crystallite, (λ = 1.54059 Å) is the wavelength of the X-rays used, β: broadening of diffraction line measured at half of its maximum intensity in radians and θ: angle of diffraction.

The maximum grain size of polycrystalline was found to be 33 nm along 200 plan to the sample with doping ratio of x = 0.5 wt.%, as revealed in Fig (2).

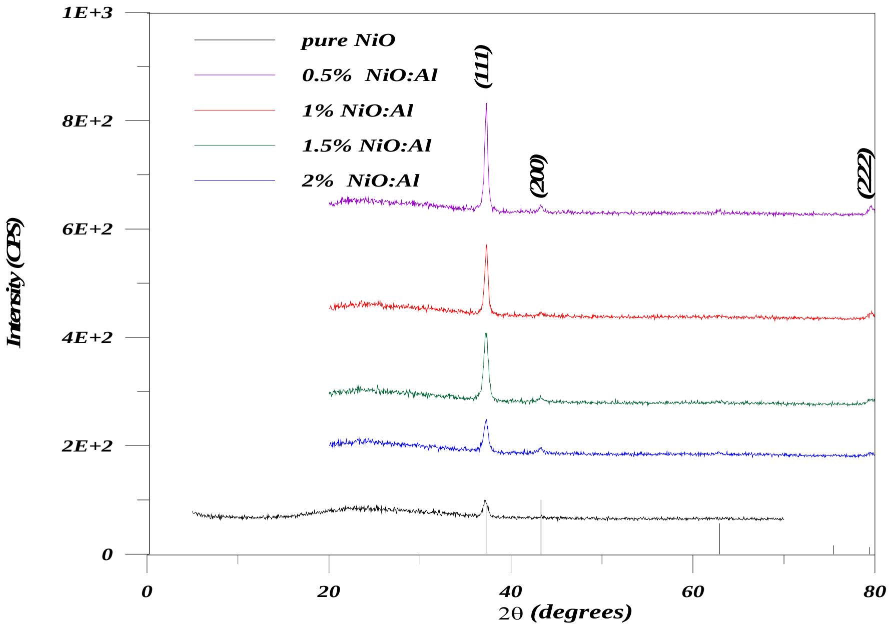


Figure 1: XRD analysis of undoped NiO and NiO:Al samples

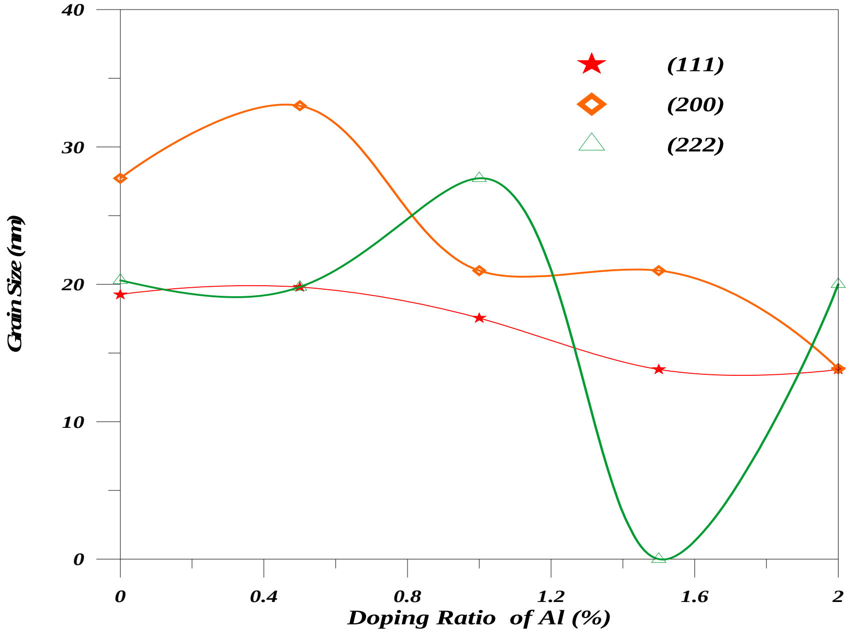
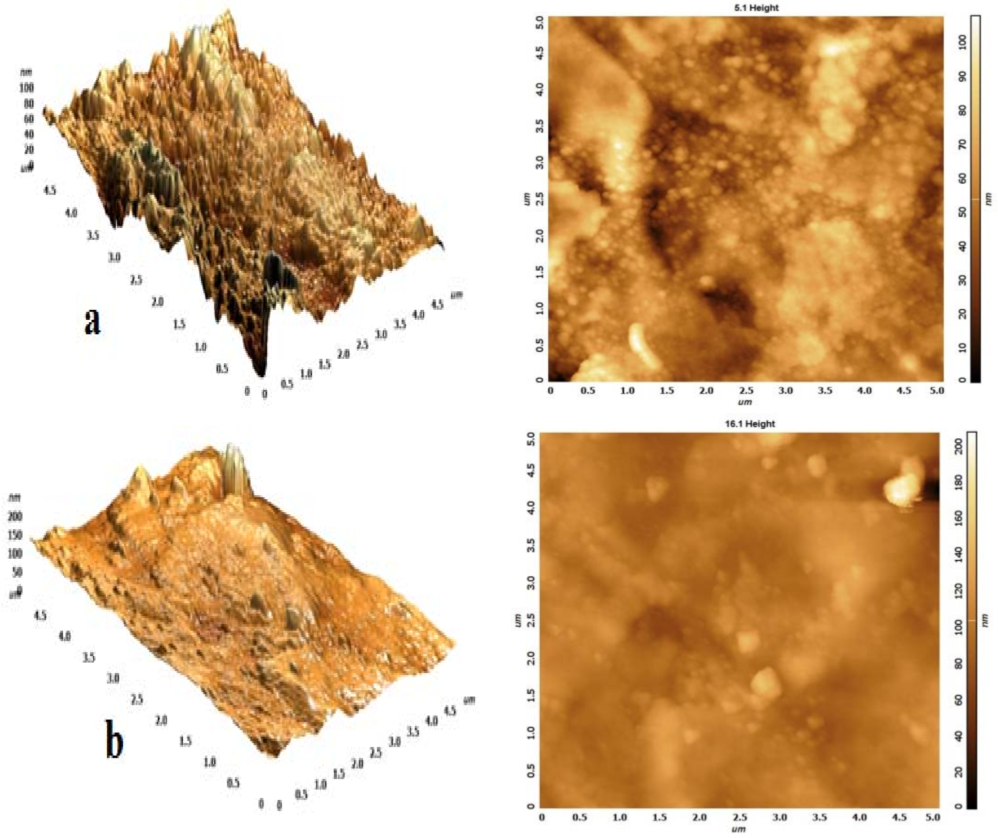
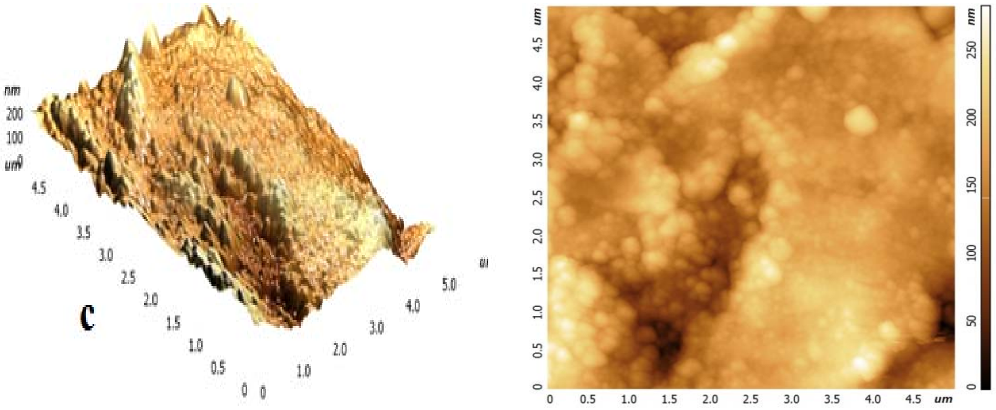


Figure 2: Illustration of the crystalline size of the doping ratio of NiO:Al

B. Morphological properties: -

Atomic force microscope (AFM) is used to study the morphology of films. The images of the NiO:Al films synthesized at different doping concentrations (x = 0.5, 1, and 2%) are shown in Fig (3).





3D 2D

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

AFM results displayed homogenous and smooth NiO:Al films. The average grain size, average roughness, and root mean square (RMS) roughness for NiO:Al films, founded from AFM, which is given in Table 1. Maximum doping ratio has enlarged the grain size and RMS roughness of the film. The increase of the grain size could be caused by columnar grain growth in the structure. The results of the crystalline size gained from AFM examination are different with those found from XRD via the Scherrer equation, may be, due to that AFM results were described an exterior crystalline surface, but the XRD results were described the interior crystalline structure, as presented in table 2.

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

(x), Doping Concentration	(RMS) nm	Average grain size (nm) of AFM measurements	Maximum crystalline size (nm)	Roughness average (nm)
undoped	10.34	34	28	6.43
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

C. Sensing properties:

To study the electrical characterization of the films, the sensor element was connected in series with multimeters.

Electrical resistivity measurements were achieved using two millimeters for current and applied voltage measurements and power supply in the range of 0 –20 Volt. Gas sensing measurements have been achieved by a home-built gas sensing chamber (gas flow elements) as displayed in Figure (4), where CO gas preparation was done by the following equation:

$$HCOOH\ (\text{heat } 70\ ^\circ C + H_2SO_4) \rightarrow CO + H_2O \qquad (2)$$

The gas sensitivity of thin film element for CO gas has been calculated at room temperature. The resistance response of each sensor structure was transformed into a sensitivity value using commonly used formula (3) for the reducing and oxidizing gases.

$$S = \Delta R / R = (R_{air} - R_{gas}) / R_{air} \qquad (3)$$

where S: sensitivity, R_{air}: resistance in air and R_{gas}: resistance with gas.

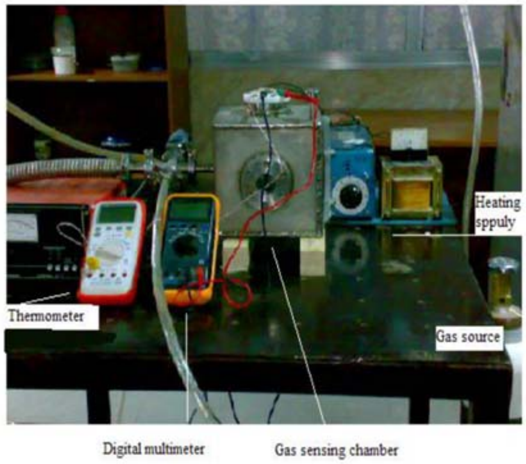
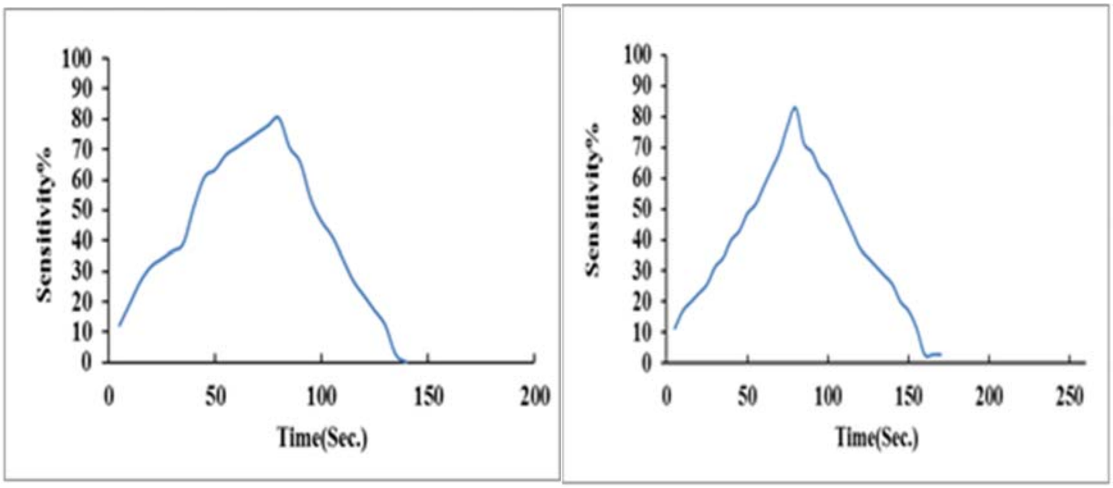


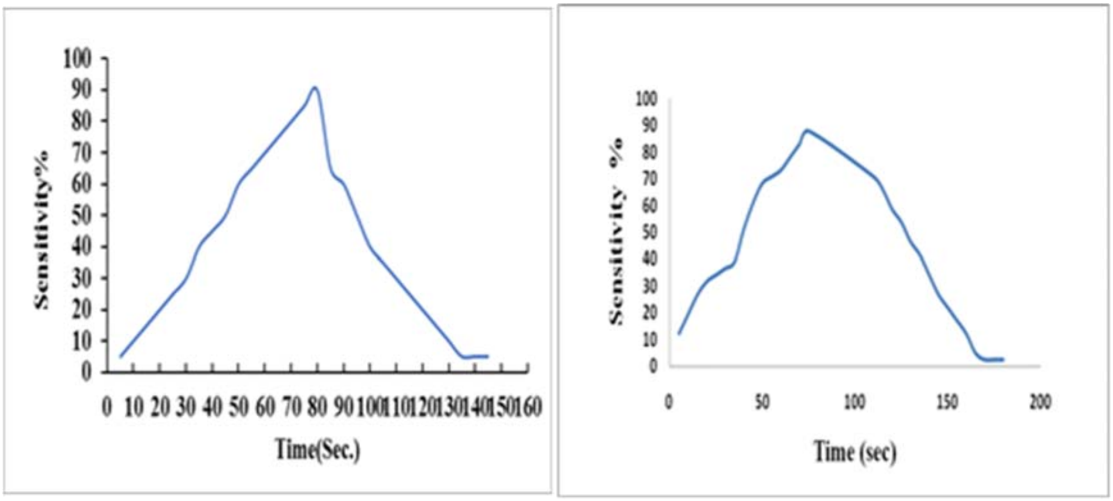
Figure 4: The gas sensing measurement setup

The sensitivity for NiO:Al thin films (0, 0.5, 1, 1.5 and 2 wt.%) was shown in figure 5.



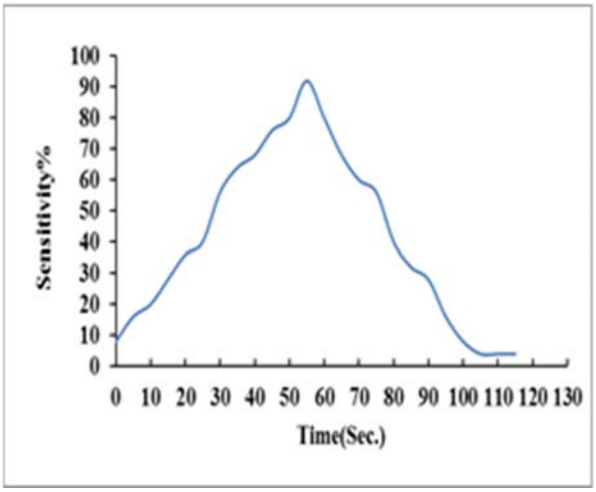
a: NiO thin films pure

b: NiO:Al thin films 0.5%



c: NiO:Al thin films 1%

d: NiO:Al thin films 1.5%



e: NiO:Al thin films 2%

Figure 5: The sensitivity for NiO:Al thin films (0, 0.5, 1, 1.5 and 2 wt.%).

The relation between maximum sensitivity and different ratios of doping is shown in Fig. (6).

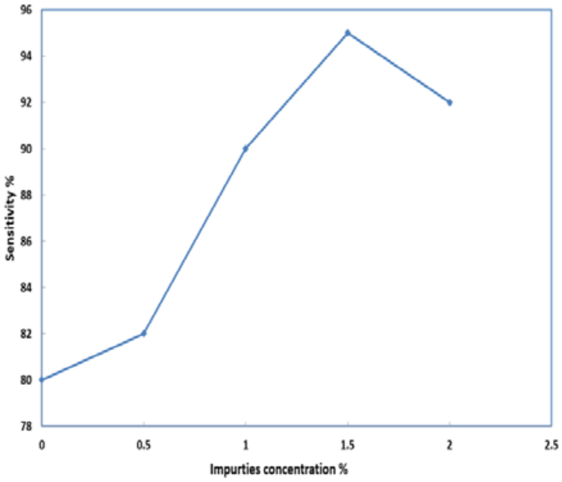


Figure 6: The relation between sensitivity and doping ratio.

Conclusions

Structural and morphological properties of pure NiO and NiO:Al thin films deposited by CVD has been studied. The structural and morphological properties showed a good agreement between XRD analysis and AFM including grain size of the films prepared. The grain sizes of NiO:Al films increased when the doping ratio of Al increased. Sensitivity was increased with increasing doping ratio too. Because of growing up in grain size and growing up in roughness, these led to decrease in resistance and increase in conductivity.

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