Effect of Doping on Structural and Electrical Properties of Titanium Dioxide (TiO_2) Thin Films for Gas Sensor

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Abstract

Undoped and nickel doped titanium oxide thin films were fabricated by spray pyrolysis by using a solution of titanium tetrachloride and ethyl alcohol. The films have been deposited on heated quartz and silicon substrates at 623 K. After annealing for 120 min at 823 K, the initially amorphous films became polycrystalline with a predominant anatase structure and average crystallite sizes depending on dopant (Ni) concentration. AFM results show that by the addition of the Ni to TiO_2 thin films they become smooth. Electrical properties have been studied by means of electrical resistivity and Hall effect measurements. The experimental result shows that nickel doping of titanium oxide thin films improve the sensor element sensitivity to NH_3 gas. The influence of variation of Ni concentration on NH_3 sensitivity of thin film sensor elements was investigated in this work. It looks promising to use the inexpensive nickel-doped titanium oxed thin films obtained by spray pyrolysis in smart gas sensing devices that are able to or recognize gas species in low concentration.

Keywords: TiO_2, spray pyrolysis, Ni dopant , gas sensor.

1. Introduction

Over the last few years a great attention has been focused on the titanium dioxide (TiO_2) thin films because its excellent materials in many applications, such as in the field of sensors, antireflection coatings, gas sensors[1], solar cells[2]and photocatalysis[3,4]. By doping, especially with transition metal atoms, these properties can be improved as desired, while keeping the films chemical and mechanical stability [1]. There are many methods that can be used to prepare TiO_2 thin films with desired properties including sol–gel[4-7], sputtering[8], anodic oxidation[9-14], pulsed laser deposition (PLD)[15], and spray pyrolysis[1-3,16-18]. Of all the afore-mentioned thin film fabrication methods, spray pyrolysis is widly used be cause of its simplicity, cheap chemical deposition procedure, allowing the growth of rough-surface films at atmospheric pressure, on large area. By this method, dopants can be easily introduced into the matrix of the film by using appropriate precursors [1, 16]. In this paper we have investigated the effect of nickel doping on structure, and electrical properties of TiO_2 thin films for using as gas sensor for NH_3 gas.

2. Experimental

Undoped and nickel-doped titanium oxide thin films were deposited on heated quartz and silicon substrate (623 K), by spraying an appropriate solution from a sprayer, placed at 30 cm in front of the heated substrate holder. The starting solution was prepared by using (2 ml) titanium tetrachloride ($TiCl_4$, purity 99.9%, 1.726g/cm3 density) which is made in "England" dissolved in (20 ml) ethyl alcohol (96%). Filtered air was used as a carrier gas, the deposition time was set to 5 sec, the samples were annealed at 823 K in air for 120 min. Salt[$NiCl_2.6H_2O$] a reused to dope TiO_2 films for different percentages (1,2,3,4 and 5%) of dopant. The structural properties of the prepared films were studied by X-ray diffraction measurements (Philips PW 1050 X-ray diffractometer, with CuKα radiation (λ= 1.54059 Å)). Morphology of the deposited TiO_2 thin films was revealed using atomic force microscopy (AFM) using a scanning probe microscopy (CSPM-5000). After annealing in the air the electrodes were deposited onto film surface by thermal evaporation of aluminum in vacuum system. To study the electrical characterization of the TiO_2 films, electrical resistivity measurements were performed using two point probe method. The type of conductivity exhibited by Hall Effect [device of type (HMS-3000)] was used to measure concentration (n), mobility and Hall coefficient (R_H). The sensitivity tests were carried out in a homemade testing chamber that measures the surface resistance of the samples. The sensing characteristics of the sensor were then observed by measuring the electrical resistance change of sensor when the latter was exposed to NH_3 gas. Under the exposure of reducing gas such as NH_3 (in the present study), its resistance decreases.

3. Results and Discussion

The crystal structure of TiO_2 films was investigated through X-ray diffraction (XRD). The X-ray diffraction spectrum of TiO_2 films pure and doping with nickel for different doping concentration (1,2,3,4 and 5 %) deposited on quartz substrate at annealing temperature(823 K) for (120min) are shown in figure (1). It is found that all the films are polycrystalline with a tetragonal crystal structure. All films show diffraction peaks belong to anatase A (101),A(004) and A (200). The diffraction peaks are in good agreement with those given in JCPD data card (JCPDS no .21-1272) for anatanse phase. The XRD results reveal that the annealed thin film at 823 K for 120 min of TiO_2 have a good crystalline. And it is observed that the pure TiO_2 films exhibit a polycrystalline having (101), (004) and (200) planes of high peak intensities. The doped titanium oxide films become less crystalline than undoped sample, the grain size was calculated from the full width at half maximum (FWHM) (β) of the preferential orientation diffraction peak by using the Scherrer equation [16]

$$D = k\lambda / (\beta \cos\theta) \qquad (1)$$

3.1 X-Ray Diffraction study.

where D is the crystallite size, k is a fixed number of 0.9, λ is the X-ray wavelength, θ is the Bragg's angle in degrees, and β is the full-width-at- half maximum (FWHM) of the chosen peak. Compared to the reference data from TiO_2 (JCPD) card, the peaks in the X- Ray diffraction shift into the region of higher 2θ, indicating stress in the grains. Increasing in full-width at half- maximum (FWHM) of (101) peak means decrease grain size of film with the increase doping concentration in TiO_2 films as shown in figure (2). XRD analysis also did not detect the dopant phase, these due to the low concentration of dopants of TiO_2:Ni at different doping concentration on the films structure are given in table (1). Increases in doping concentration in TiO_2 films result in the increasing lattice constant (a) ,this can be attributed to increase in interplanar distance (d) according to equations (2). And Increases in doping concentration in TiO_2 films approaching the lattice constant ratio from the stress free TiO2 (2.5142 Å), where in the case of films dopping with 5% Ni the ratio of lattice constant c/a was (2.5087 Å) as shown an figure (3).The lattice constants 'a' and 'c' of the tetragonal structure of TiO_2 can be calculated using the relations (2) & (3) given below[4,19].

$$a = b = 2 * d_{200} \qquad (2)$$

$c = 4 * d_{004}$ (3)

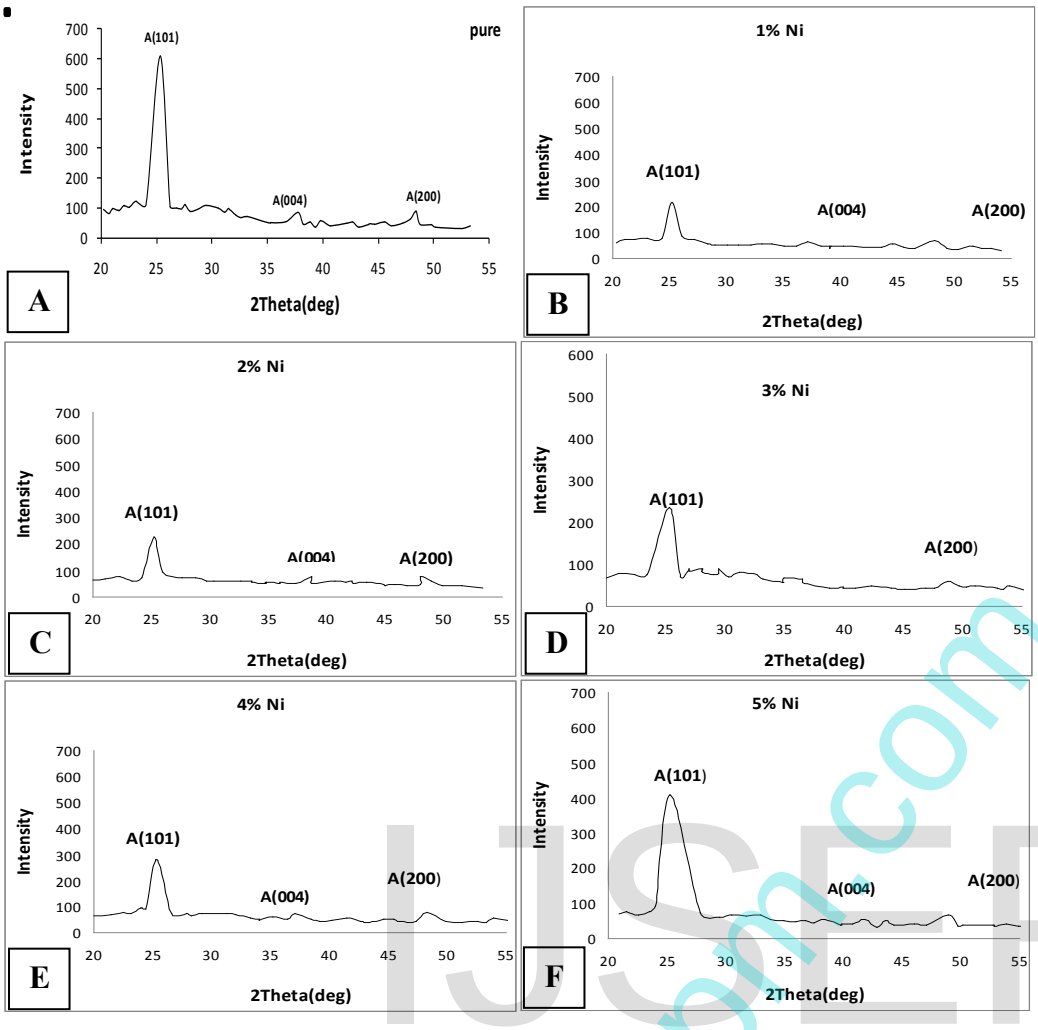

Fig. (1) : XRD patterns of TiO_2 films pure and doping with nickel at different concentrations(A) TiO_2 pure (B) 1%Ni (C)2% Ni (D)3% Ni (E)4% Ni (F)5% Ni.

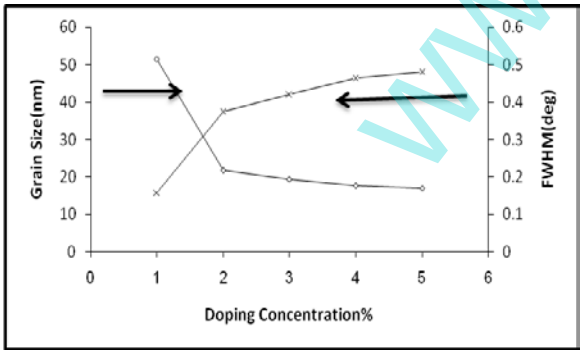

Fig. (2) :The m ain gr ain s ize a nd Full W idth a t Half M aximum (FWHM) f or TiO_2 A (101) at different doping concentration for nickel.

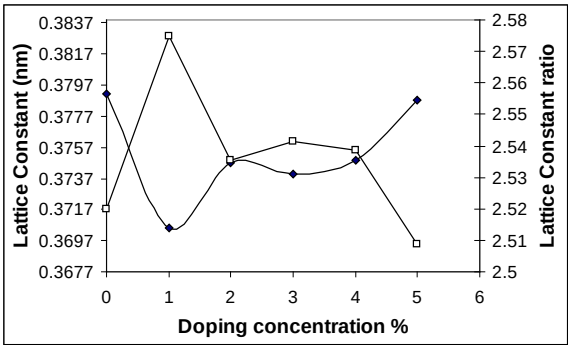

Fig. (3) :Lattice constant (a) a nd la ttice c onstant ratio (c/a) a t di fferent do ping concentration for nickel.

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Table(1): Experimental results for TiO_2 pure and doping with nickel at different doping concentrations.

TiO_2 doping with nickel	*2(θ) deg*	*hkl*	*β (deg)*	*Grian size (nm)*	*a=b (nm)*	*c (nm)*	*c/a*
Undoped TiO_2	25.27	A(101)	0.272	29.87	0.37914	0.958989	2.52
1% Ni	25.15	A(101)	0.15840	51.386	0.3705	0.95432	2.575
2% Ni	25.2	A(101)	0.37540	21.68	0.374722	0.950152	2.5356
3% Ni	25.3	A(101)	0.4200	19.400	0.374014	0.950472	2.5412
4% Ni	25.34	A(101)	0.46360	17.56	0.374888	0.951704	2.5386
5% Ni	25.38	A(101)	0.48120	16.92	0.37874	0.950168	2.5087

3.2. AFM Study

The surface morphology of TiO_2 thin films was analyzed using atomic force microscope. Figure (4) shows the typical three - dimensional AFM image of TiO_2 and doping TiO_2 with nickel films deposited at annealing temperature 823 K and annealing time 120 min on quartz substrate by using spray pyrolysis technique. AFM results show that by the addition of the Ni to TiO_2 thin films they become smooth where the root mean square (RMS) (nm) for undoped and doped with Ni are 0.1658 nm and 0.115 nm respectively.

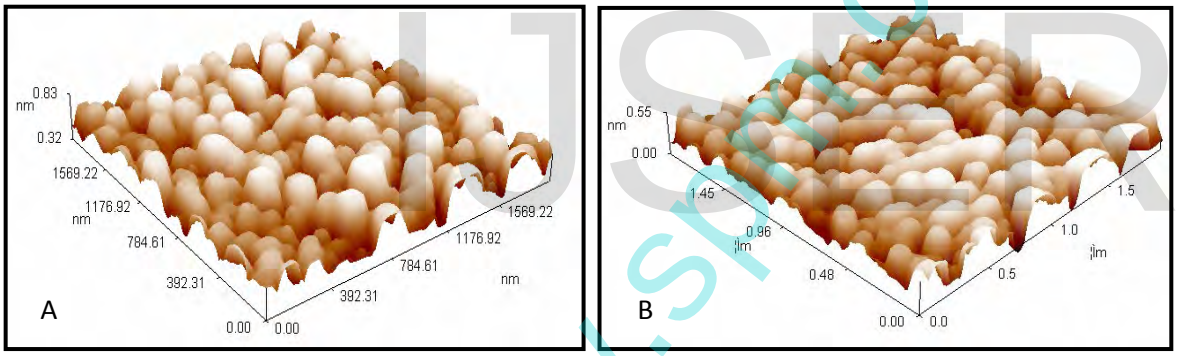

Fig. (4) :The AFM images: (A)undopped TiO_2 annealing at 823 K and 120 min (B) TiO_2 doping with nickel at 5%.

3.3. Electrical properties

In order to investigate the effect of nickel doping on some electrical properties of TiO_2 films, electrical resistivity as a function of doping concentrations Ni as shown in figure (5). Shows that the electrical resistivity is decreases with increasing doping concentration (Ni) in TiO_2 thin films could be attributed to the increasing concentration (n).

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Electrical resistivity is a function of temperature for different doping concentrations as shown in (6). The electrical resistivity was found to decrease with increasing doping concentration in TiO_2 thin films. Table (2) shows the activation energy E_{a1} and E_{a2} of the TiO_2 thin films doped with nickel. It is clear that the activation energies E_{a1} and E_{a2} increase with increasing doping concentration in the films

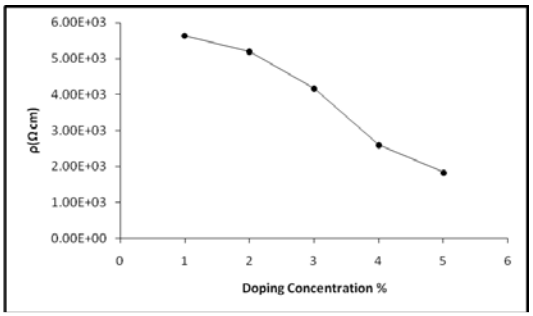

Fig. (5): The electrical resistivity as a function of different doping concentration with nickel.

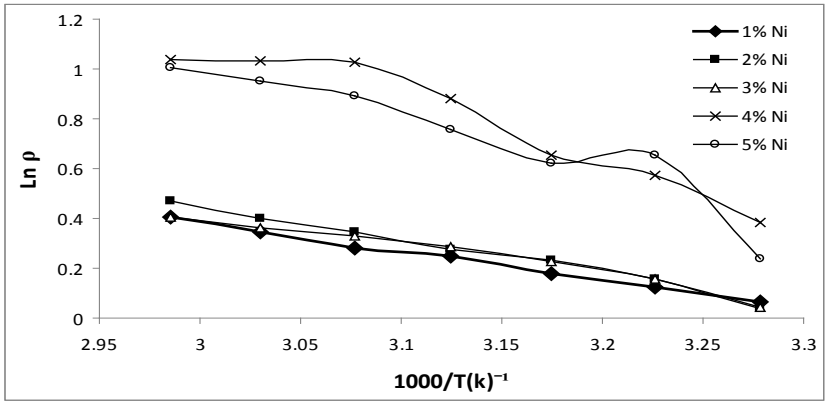

Fig. (6): Ln ρ as a function of 1000/T(K) $^{-1}$ for TiO_2 films at different doping concentrations with nickel.

Table(2) : A ctivation en ergies E a_1 and E a_2 for TiO_2 do ping w ith nickel at different doping concentrations.

Doping with nickel	E_{a1}(ev)	E_{a2}(ev)
1% Ni:TiO_2	0.0182	0.06020
2% Ni:TiO_2	0.03126	0.0894
3% Ni:TiO_2	0.20273	0.09759
4% Ni:TiO_2	0.2670	0.11267
5% Ni:TiO_2	0.2919	0.11396

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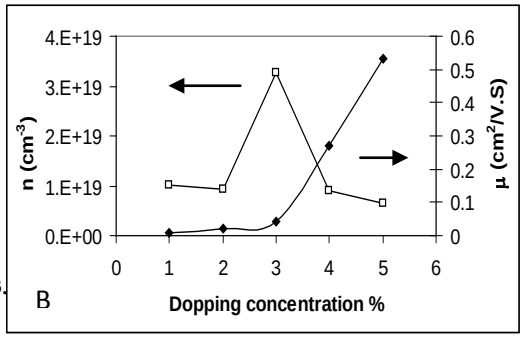
3.4. Hall Measurment

The r esults o btained f rom H all e ffect f or n ickel d oping TiO_2 and fixed a nnealing t emperature at 550°C for 120 min w ere (n-type). The results h ave s hown t hat a g reater increase i n t he v alue o f el ectrical conductivity, a ccompanied b y a clear i ncrease i n the v alues o f charge carriers with th e d ecrease in th e v alues o f b oth th e mo bility a nd H all coefficient. The value of (R_H) de creases w ith the i ncreasing o f doping concentration in the films as shown in figure (7). H all coefficient s ign has not be en c hanged by t he i ncrease in do ping c oncentration. W hich indicates that the electrons are the charge carriers and are responsible for the increased conductivity, as shown in table (3). The mobility decrease with increasing doping concentration in TiO_2 thin films .The results may be attributed to the average grain size decreasing with increasing doping concentration in th e f ilms (as s hown by X - ray d iffraction). T herefore doping concentration in TiO_2 the films plays a vital role in determining its electrical properties.



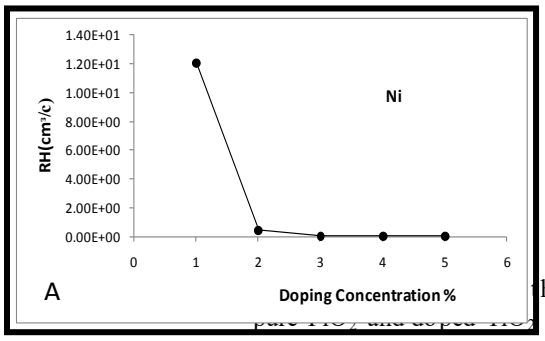


Fig. (8):

(A) The carrier concentration and mobility of TiO2 as a function of doping c oncentration for N i. (B)Hall c oefficient of T iO_2 as a function of d oping c oncentration for Ni.

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are shown with time. The resistance of pure TiO_2 films and films doped varies with noble metal (Ni) in different concentrations (1 %, 3% and 5%). The resistance decreases with increasing doping concentrations due to increase in the sensing of the TiO_2 films. A minimum resistance is of TiO_2 doped with (5%) noble metal. The resistance decreases drastically during the gas exposure, a maximum resistance started to increase in TiO_2 pure. The gas sensitivity of undoped and doped TiO_2 films is calculated from measuring the resistance change in thin films in air and in gas. The change in surface resistance in presence of gas (NH_3) with time is measured by using equation (4). Figure (8) shows the gas sensitivity of undoped TiO_2 and doped with nickel. It can be seen from this observation that the sensitivity values of all samples increase with time. The sensitivity of the metal oxide semiconductor sensor is mainly determined by the interaction between the target gas and the surface of the sensor. The greater surface area of the materials stronger interaction becomes between the adsorbed gases and the sensor surface, higher gas sensing sensitivit. The sensitivity value of pure TiO_2 is less than sensitivity of doped TiO_2 because the surface species and trapped electrons are returned to the conduction band causing an increase in the conductivity of the TiO_2 films doped with noble metal and the sensitivity of the sensor increases.

$$S=(R_g-R_a/R_a)100\% \qquad (4)$$

where R_g is the sensor resistance influenced by the NH_3 gas, R_a the sensor resistance in the air[18].

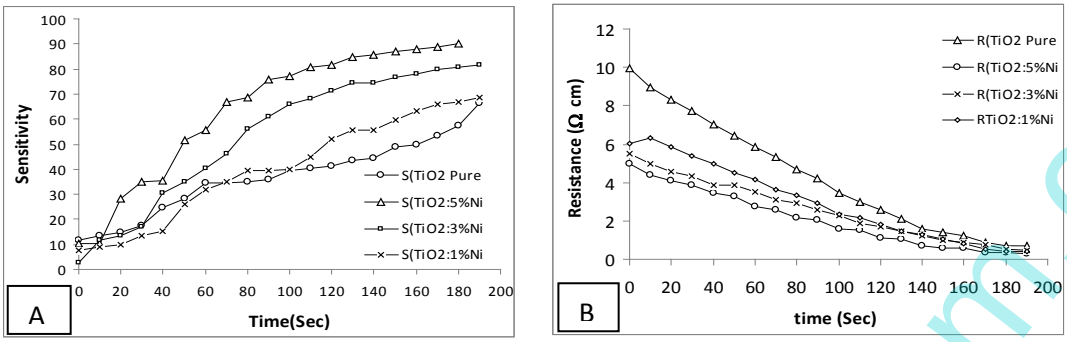

Fig. (8): (A)Resistance of TiO_2 pure and doped with nickel as a function of operation time for NH_3 gas .(B) :Sensitivity for TiO_2 pure and doping with nickel films for NH_3 gas at different operation time.

4. Conclusions

We have successfully prepared doped n-TiO2 thin films using titanium tetrachloride and ethyl alcohol by employing a simple and inexpensive spray pyrolysis technique. Influence of nickel dopant on structure, morphological, and electrical properties is discussed. XRD shows that as- deposited films are amorphous and became polycrystalline with anatise crystal structure, oriented along (101) plane upon annealing at 823 K. These experimental results confirm that conductometric gas sensors based on nickel-doped TiO_2 as sensitive layer for NH_3 gas detection.

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