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The Effect of Al Doping on the Sensitivity of SnO_2 Films Prepared by Chemical Spray Pyrolysis

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Abstract
Pure and Al-doped SnO_2 as gas sensors with properties characteristics provoking gas sensitivity were used for measuring CO_2 atmospheres. In this paper we discussed the optical properties of undoped and Al (each 3, 5 and %) doped SnO_2 thin films were synthesized by spray pyrolysis on glass substrate. The samples were characterized using X-ray diffraction (XRD) and gas sensitivity. The XRD analysis reveals that the Al dopants were substituted into rutile SnO_2 nanoparticles without forming any secondary phase. The average particle size of the samples was increasing with increasing Al concentration. From XRD and AFM micrograph it was confirmed, the grain size in the range of 22.4-34.4 nm. The study reveals polycrystalline structure with prominent peaks. In particular, 7% Al-SnO_2 films have a higher sensitivity (30%).
Keywords: Structural, gas sensitivity properties, Aluminum (Al) doped , Tin oxide (SnO2)
nanocrystal.
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Introduction

The tin oxide is a wide bandgap semiconductor (energy bandgap 3.6 eV), and it has only the tin atom that occupies the centre of a surrounding core composed of six oxygen atoms placed approximately at the corners of a quasiregular octahedron (Figure 1). In the case of oxygen atoms, three tin atoms surround each of them, forming an almost equilateral triangle. The lattice parameters are $a = b = 4.737$A° and $c = 3.186$A° [1].

Among the metal oxide sensors, SnO_2 has been the most studied sensitive layer. SnO_2 is a typical n-type semiconductor.

SnO_2 thin films have been deposited using different techniques, such as spray pyrolysis [4], sol-gel process [5, 6], chemical vapour deposition [7], sputtering [8], and pulsed laser deposition [9]. Of these methods, the spray pyrolysis is unique and cost effective compared to other methods requiring high vacuum environment. It is one step method operating at atmospheric pressure with very short production time [12]. SnO_2 has been identified as a potential semiconductor material with many applications, including acting as a supercapacitor [8], catalyst [9], energy storage [10] and as gas sensor [11]. SnO_2 owing to a wide bandgap is an insulator in its stoichiometric form. However, due to the high intrinsic defects, that are oxygen deficiencies, tinoxide ($SnO_2{-}X$) possesses a high conductivity. It has been shown that the formation energy of oxygen vacancies and tin interstitials in SnO_2 is very low. Therefore, these defects form readily, which explains the high conductivity of pure, but nonstoichiometric, tin oxide. Studies show that the morphology, structure and size of metal oxide materials have been proven to influence the sensing performance of SnO_2 [12].

Metal oxide semiconductor (MOS) sensor technology is based on the change in resistance of a sensitive metal oxide layer which is induced by the interaction between a surface and ambient gases. Since the last decade there has been a great deal of interest in the preparation of inexpensive thin films of SnO_2. This is because tin dioxide based thin films with large band gap ($Eg > 3$ eV) *n*-type semiconductors are attractive from the scientific and technological point of view [5]. The technique involves a simple technology in which an ionic solution (containing the constituent elements of a compound in the form of soluble salts) is sprayed over heated substrates.

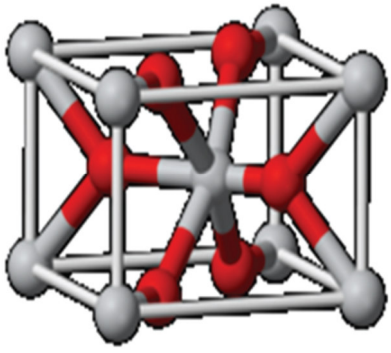


Figure 1: The rutile structure of SnO_2, which contains tin atoms at the corners and center of the unit cell.

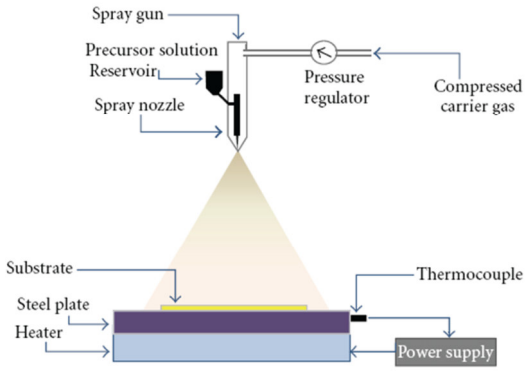


Figure 2: The scheme of the spray pyrolysis setup.

In this work $AlCl_3$ doped SnO_2 synthesis with different concentration and study the effect of doping on the structural parameters and sensing properties of the samples by X-ray diffraction (XRD), atomic force microscopy (AFM), and gas sensor system.

Experimental

The SnO_2 films were doping with Al (3%, 5%, 7%) prepared by spray pyrolysis. It was observed that the growth rate of SnO_2 films prepared from $SnCl_4 \cdot 5H_2O$ was higher and their resistance lower in comparison with those prepared from anhydrous $SnCl_4$ [1]. Thin-film deposition, using the spray pyrolysis technique, involves spraying a metal salt solution onto a heated substrate (Fig. 2). Droplets impact on the substrate surface, spread into a disk shaped structure, and undergo thermal decomposition. The shape and size of the disk depends on the momentum and volume of the droplet, as well as the substrate temperature.

The glass substrate prepared in 2x2 cm^2 dimensions were subsequently cleaned in ethanol, followed by washing with distilled water with ultrasonic for 10 min with heating. The cleaned substrates were placed on a hot plate at a constant temperature of 300°C. The precursor solution used was of 0.1M concentration of $SnCl_4 \cdot 5H_2O$ dissolved in distilled water. The atomization of the solution into a spray of fine droplets was carried out by the spray nozzle and compressed N_2 was used as the carrier gas.

The various process parameters used in the film preparation are listed in table1. During the optimization of the process parameters, the substrate temperature was found to be the most important parameter in the film preparation for gas sensing applications.

The as-deposited SnO_2 films were characterized by structural techniques. The chemical and structural phases of the SnO_2 thin film was determined by x-ray diffractometer (Cu- Kα, λ=1.5418 Å) over a 2θ range of 10°-70°[Shimadzu Lab XRD 6000]. The morphology is observed by Atomic Force Microscope AFM (Digital Instruments, Nanoscope III USA) Scanning Probe Microscope (AA3000) was used.

Table (1) Process parameter for SnO_2 films.

Spray parameter	Optimum value
Solution concentration	0.1M
Carrier gas	N_2
Nozzle	glass
Nozzle-substrate distance	25 cm
Solvent	Distilled water
Solution flow rate	4 ml/min
Gas pressure	
Substrate temperature	300°C

The surface morphology was studied by atomic force microscope (AFM). The gas sensing chamber had been employed for testing of the films to gases. The heater was placed around the champer to heat the sample under test up to required operating temperature (50-200) °C. The current was measured using a digital Multimeters (HANTEK365). Films response to CO_2 gas was studied by introducing the gas of known concentration (4%) volume ratio to the air and recording resistance as a function of time.

Result and discussion

The glass substrate was ultrasonically cleaned by keeping in distilled water, for 10 min, respectively. The films were deposited on the glass substrates by locally fabricated spray pyrolysis system. In order to prepare the coating solution, 1.99 gm $SnCl_4.5H_2O$ [99%Merck, Germany] was added with 100 ml water by heating at 80°C. The concentration of the sprayed solution was 0.1M, for precursor solution of pure SnO_2 thin film. In order to prepare the Al doped films, $AlCl_3$ [99%BHD, Germany] were dissolved in 10 ml of distilled water with different

doping ratio% and the solutions were added into the coating solution, respectively.

$$SnCl_2+2H_2O \xrightarrow{\text{Heat}} SnO_2+4HCl$$

The films were found almost transparent. In this work, the thicknesses of films were found to be 100nm.

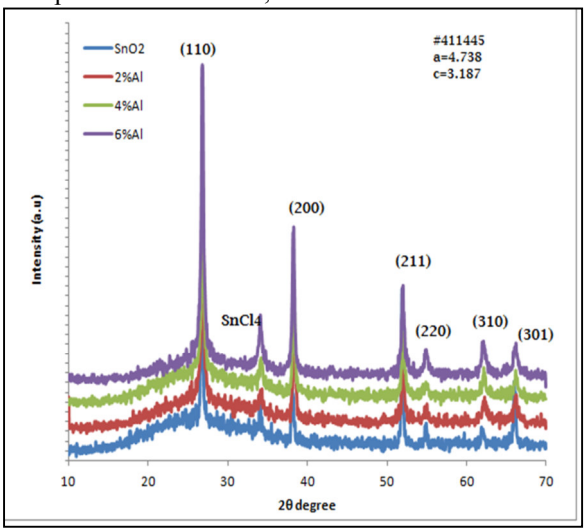


Fig (3): XRD images for pure and 3%, 5% and 7% Al doped SnO_2 thin film

Table2. Lattice parameters and crystallite size values of SnO_2 films prepared for various doping atoms.

Doping atom	a(Å)	C(Å)	c/a	D(Å)
Undoped	6.648	4.700	0.707	33.58
3%Al	6.637	4.693	0.707	20.12
5%Al	6.634	4.691	0.707	27.00
7%Al	6.628	4.687	0.707	27.11

The XRD patterns of SnO_2 and Al doped films are shown in Fig.3. The films deposited showed sex peaks namely (110), (200), (211), (220), (310) and (301). Since all the peaks are sharp it is evident that the films deposited are polycrystalline in nature and the positions of X-ray diffraction peaks fit well with the tetragonal structure of SnO_2 (JCPDS card SnO_2, 41-1445). The dopants do not from extra peaks in the XRD pattern in doped SnO_2 films because dopant atoms incorporate homogeneously into the SnO_2 matrix. In literature published on SnO_2 films doped with different atoms such as Al exhibited similar behaviors [2]. For Al doped SnO_2 the peaks become wider due to their intensity decreases and shifted to lower diffraction angle with the increases of the Al concentrations this is due to the substitution of Sn^{+4} ions at the lattice sites with the Al^{+3} ion.

The lattice parameters of SnO_2 decreased after Al doping as shown in (Table 2). The observed variation in lattice parameters is consistent with the smaller radius of the Al^{+3} ions. For the tetragonal structure, lattice parameters can be calculated from:

$$1/d_{hkl}^2 = h^2 + k^2/a^2 + l^2/c^2$$

Where h, k, and l are all integers, (hkl) is the lattice plane indices, a and c are lattice constants. The crystallite size (D) of undoped and Al doped SnO_2 powder for all the dopant samples were calculated using Debye-Scherrer formula [3]:

$$D = k\lambda/\beta \cos\theta$$

Where k is a constant, λ is the diffraction wavelength of Cu Kα (λ = 1.5406 Å), β is the full width at half maximum (FWHM), and θ is the angle of diffraction.

Atomic force microscopy (AFM) is a useful technique to determine the surface morphology and particle size of the samples. Figure 4 show the 2D AFM images and particle distribution of pure and Al doped SnO_2. Its images for pure and doped SnO_2 revealed semispherical shapes, their particle distribution is uniform and particle size reduces with the increasing of the Al concentrations. Roughness decreases with increases of doping concentration. The size of the particles obtained from (AFM) images is the largest to those values obtained from measurements of (XRD) due to the one consists of crystallite, and your (AFM) photographed the top surface of the granules either apparatus (XRD) gets diffraction from surfaces of crystalline which are each a crystallization of microscopic size. Area roughness of the prepared samples values are:, 13.77 nm,22.45 nm, 23.37 nm and 34.14 nm for pure and doped SnO_2, as shown in figure 5.

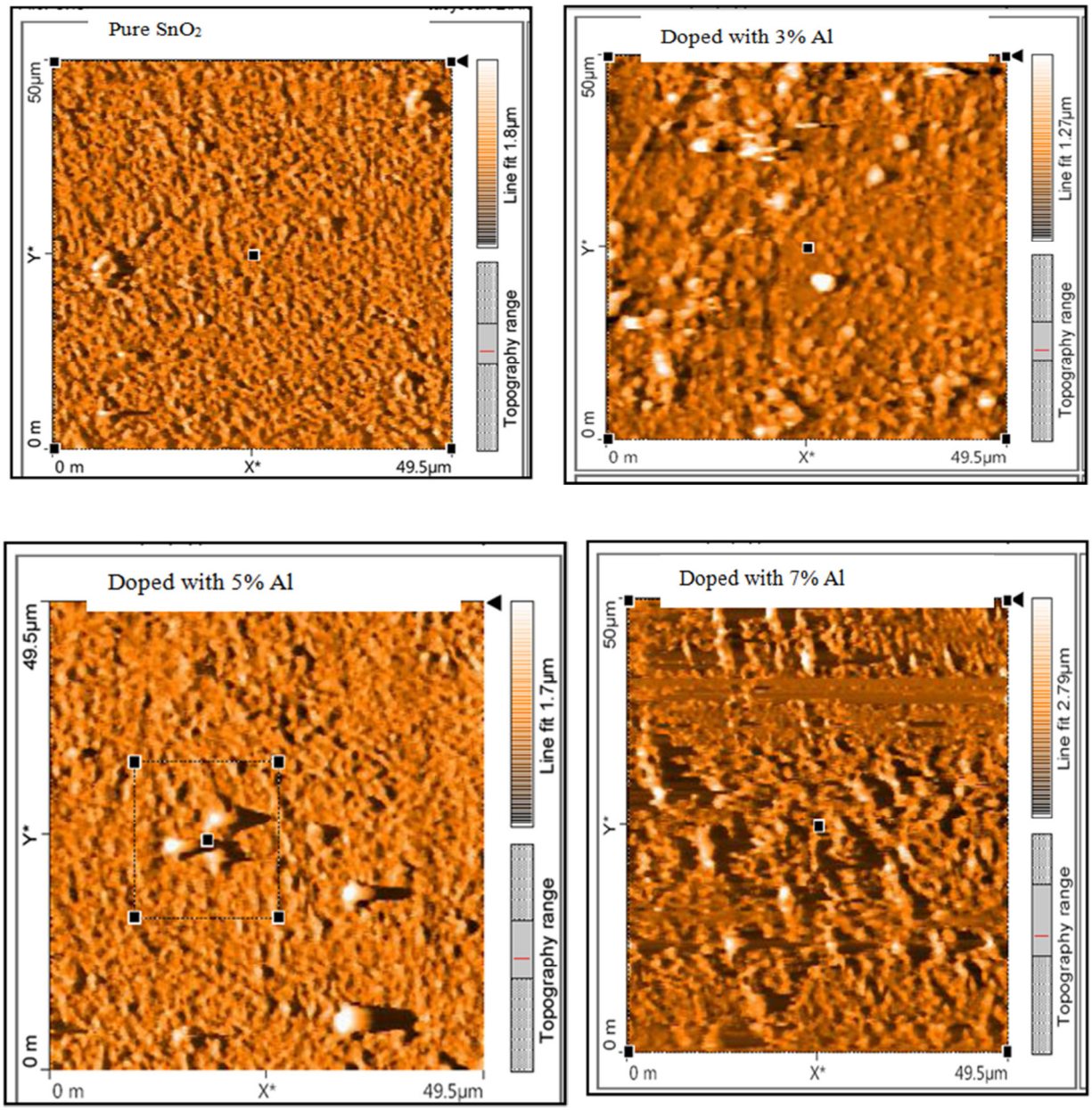


Fig 4: AFM 2D, image and the particles distribution for pure and doping SnO_2.

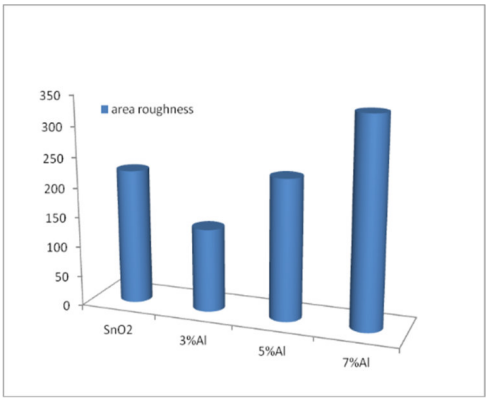
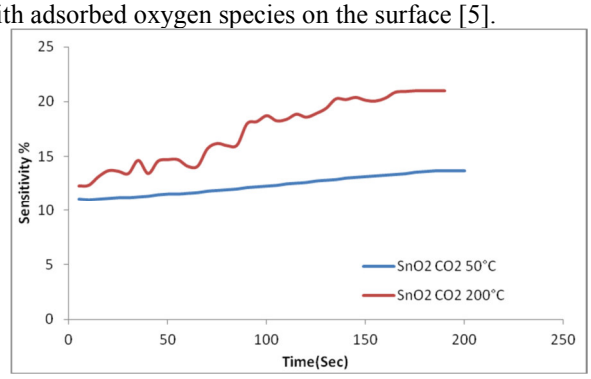


Fig (5): doping effect on area roughness of SnO_2

The gas sensitivity of SnO_2 thin film to CO_2 gas has been studied. The gas sensitivity of SnO_2 films is calculated from measuring the resistance change in thin films in air and in CO_2 gas.

The mechanism of sensing oxidizing gas by SnO_2 is elucidated as: when in contact with an oxidizing gas (electron acceptor), such as CO_2, the negatively charged oxygen (O^-) absorbed on the SnO_2 films surface will react [4]. The reaction between the oxidizing gas and (O^-) leads to an increase of the hole density in the surface charge layer and decrease of the SnO_2 resistance. Figure (6,9) show the films sensitivity of undoped SnO_2 and doped with 7%Al, we can see the sensitivity is increase with increasing operating time and reaches to a saturation limit. Then, the sensitivity returns back to its original value in several minute after stopping the exposure of gas. At low working temperature the low sensor response can be attributed to the low thermal energy of CO_2 molecules to react with adsorbed oxygen species on the surface [5].



Fig(6): Dynamic sensitivity to CO_2 gas at 50°C and 200°C for pure SnO_2

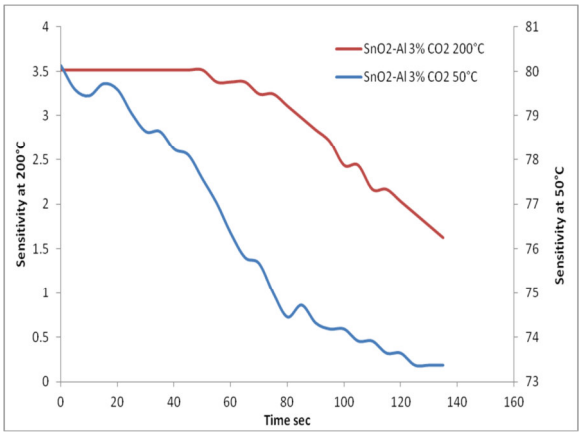


Fig (7): Dynamic sensitivity to CO_2 gas at 50°C and 200°C for pure SnO_2-3%Al

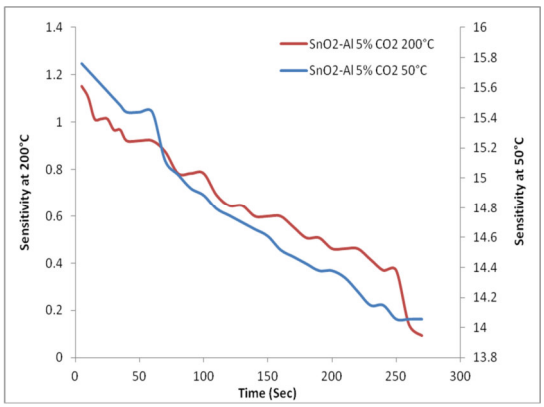


Fig (8): Dynamic sensitivity to CO_2 gas at 50°C and 200°C for pure SnO_2-5%Al

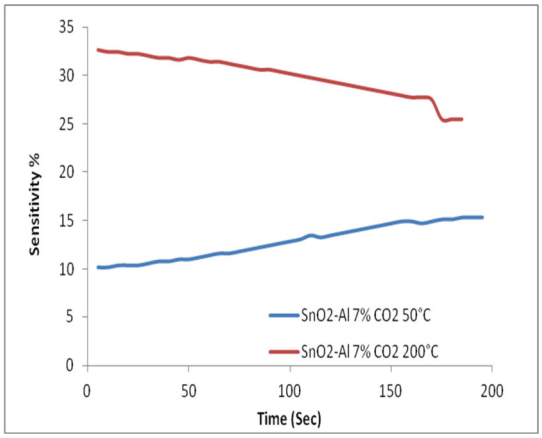
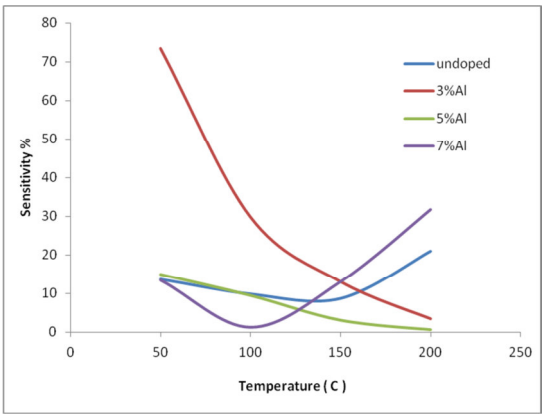


Fig (9): Dynamic sensitivity to CO_2 gas at 50°C and 200°C for pure SnO_2-7%Al



Fig(10): Effect of temperature on the sensitivity of SnO_2 (3%, 5%, 7%) Al and pure SnO_2.

Fig (7,8) shows the effect of temperature on the sensitivity of pure SnO_2 and doping with operating temperature in 3% and 5% doping of Al and pure SnO_2. While the sensitivity of pure SnO_2 and doped at 7%Al to CO_2 gas reached a maximum at 200°C, while 3%Al and 5%Al doping decrease of sensitivity with increase of temperature.

We think that the Al doping effect obtained by us is related with surface oxygen in the tin oxide thin films. It is known that the electrical resistance is controlled by chemisorption of oxygen in the metal oxide films in oxygen rich atmosphere [6].

However, the sensitivity of 3%Al-SnO_2 films (73.37%) is greater than the sensitivity of 7% Al-SnO_2 films (13.46%), this may be due to the deactivation of the surface area of SnO_2 films, as shown in figure 10.

Conclusion

In this paper, the undoped and Al-doped SnO_2 thin films were synthesized by the spray pyrolysis method. The various measurement equipments were used to characterize their structural and sensing. The changes in resistance of undoped and Al-doped SnO_2 thin films during the injection of CO_2 gas show a high sensitivity in a short time.

The presence of Al in the SnO_2 favored in decrementing the barrier height, which increased the conductivity and further sensitivity. Additionally, the copper-incorporation-produced undulations accelerated the oxygen adsorption and, subsequently, decreased the response and recovery times of the sensor.

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