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Effect of Mixing Ratio of $(\text{SnO}_2)_{1-x}(\text{In}_2\text{O}_3)_x$ Thin Film on Gas Sensitivity

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Effect of Mixing Ratio of $(\text{SnO}_2)_{1-x}(\text{In}_2\text{O}_3)_x$ Thin Film on Gas Sensitivity

Abstract

In this work, Nitrogen dioxide gas sensor was manufactured from SnO_2 and $(\text{SnO}_2)_{1-x}(\text{In}_2\text{O}_3)_x$ at different atomic ratios ($x=0.05, 0.1$ and 0.15) using pulsed laser deposition technique. The effect of the preparation ratio on structural properties, surface topography, optical and electrical characteristics and gas sensor efficiency were studied. The x-ray diffraction measurements showed polycrystalline structures for all samples and their crystallite size decreases with increasing the doping ratio. The AFM measurement illustrates spherical SnO_2 shapes converted to filament-like shapes at $x=0.1$, and that the average particle diameter decreased, while the RMS roughness increased with increasing ratio. The best samples in terms of gas sensitivity were produced at the 0.1 ratio due to the associated with low particle sizes and high charge carrier concentration. The highest gas sensitivity appeared at 200°C operating temperature, and it is increased with gas concentration as a second-order equation and be nearly stable at 400 ppm NO_2 gas. The best sample appeared at 10% $\text{In}_2\text{O}_3:\text{SnO}_2$ atomic ratio.

Keywords

gas sensor, metal oxide, pulse laser deposition, thin film

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1. Introduction

Nowadays, there is considerable interest amongst researchers to fabricate devices for gases detection to meet the needs of occupational safety with regards to hazardous gases, or for the purposes of environmental pollution control, thus helping to protect organisms from harmful gases [1]. Chemisorption gas sensors, especially based on metal oxides semiconductor, are a promising target as they generally show good sensitivities at low cost. Tin (IV) oxide (SnO_2) is one of the best such metal oxides gas sensors, whose operation is based on the principle of changing the sample impedance when exposed to target gas due to the variation in oxygen species adsorbed on its surface [2]. Gas sensors vary in their sensitivity depending on its material, preparation method, doping with other materials or by transforming them to nanostructures with different dimensions and forms [3]. The doping enhances the sensitivity of substances to specific gases and can reduce sensor response time by modifying the way in which the growth of the nanoparticles [4].

Environmentally hazardous gases are classified as oxidizing gases, such as NO_2 and CO_2 , and reducing gases, such as H_2S and CO [5]. When a metal oxide semiconductor is exposed to a reducing gas, the gas reacts with the oxygen ions on the surface of the semiconductor, releasing the electrons back into the conductivity band. Therefore, the concentration of electrons on the semiconductor surface increases, the resistance of n-type semiconductors decreases, and when exposed to an oxidizing gas, the n-type impedance increases [6].

The gas sensitivity (S) of sensors can be obtained using the relationships $|\Delta R/R_{\text{air}}|$ where the resistance variation $|\Delta R| = |R_{\text{air}} - R_{\text{gas}}|$, R_{air} and R_{gas} are the sample resistance in clean air and under target gas exposure, respectively. After closing the gas entrance the sensor recovering time period in the air was calculated [7].

In this study, we investigate the effect of the $\text{In}_2\text{O}_3/\text{SnO}_2$ atomic ratio on structural properties, surface morphology, optical properties and NO_2 gas sensing performance based on $(\text{SnO}_2)_{1-x}(\text{In}_2\text{O}_3)_x$ thin films.

2. Experimental

Tin (IV) oxide powder (SnO_2) at 99% purity from India-Mart Co. and Indium (III) oxide (In_2O_3) at 99.998% purity from Sigma Aldrich Co. were mixed in three ratios (SnO_2), $(\text{SnO}_2)_{0.95}(\text{In}_2\text{O}_3)_{0.05}$ and $(\text{SnO}_2)_{0.9}(\text{In}_2\text{O}_3)_{0.1}$ using ball mill mixer and then formed as targets of 1.5 cm diameter using a hydraulic piston. Thin films were prepared using the pulsed laser deposition technique (PLD) inside an evacuated chamber at 10^{-3} mbar pressure. The prepared films were studied via x-ray diffraction with $\text{Cu K}\alpha$ radiation (Shimadzu), UV-visible absorbance, Hall Effect measurements and by AFM (CSPM).

Aluminum comb-like electrodes were deposited on thin films surface, as shown in Figure 1, by thermal evaporation using an Edward coating (model Auto 306) under high vacuum (10^{-5} mbar).

Gas sensor specifications were tested in a chamber with a thermometer-controlled hot plate heater at different operating temperatures. A rotary pump was used to evacuate the chamber. The gas mixture (target gas and air) were admitted to the chamber in a controlled manner. The variation of sample resistance was observed using a multimeter connected to the sample electrodes, the data from which was transferred directly to a computer. The air was allowed to pass into the chamber after every NO_2 gas exposure.

Fig. 1. Schematic of chemoresistance gas sensor based on $(\text{SnO}_2)_{1-x}(\text{In}_2\text{O}_3)_x$ thin films.

Fig. 2. X-ray diffraction patterns for SnO_2 and $(\text{SnO}_2)_{1-x}(\text{In}_2\text{O}_3)_x$ thin films prepared at different ratios.

3. Results and discussions

Figure 2 illustrates the x-ray diffraction patterns for SnO_2 , $(\text{SnO}_2)_{0.95}(\text{In}_2\text{O}_3)_{0.05}$ and $(\text{SnO}_2)_{0.9}(\text{In}_2\text{O}_3)_{0.1}$ thin films deposited on glass substrates via PLD technique and annealed at 300°C . Polycrystalline structures were observed for all samples. The SnO_2 thin film, with peaks at 26.5411° , 33.8356° , 37.9110° , 51.7123° , 54.7603° , 57.8082° , 61.8493° , 64.6918° and 65.9247° matched with the (110), (101), (200), (211), (220), (002), (130), (112) and (301) orientations, respectively, corresponding to standard card No. 96-900-9083, indicating a

tetragonal structure. Essentially identical peaks appeared in the mixed samples, though with additional peaks corresponding to the cubic phase for In_2O_3 , with card No. 96-101-0589, which appeared at 30.4110° and 50.7534° belonging to the (222) and (440) planes. The intensities of these peaks were found to increase when the $\text{In}_2\text{O}_3/\text{SnO}_2$ to 10%; the associated peaks also seemed to show increased broadening, indicating a decrease in crystallite size, as measured by Sherrer's formula.

The full width at half maximum (FWHM) for peaks (which determined by Lorentzian fitting) and the crystallite size (calculated using Sherrer's

Table 1
Structural parameters for $(\text{SnO}_2)_{1-x}(\text{In}_2\text{O}_3)_x$ thin films prepared at different mixing ratios.

Sample	2θ (Deg.)	FWHM (Deg.)	d_{hkl} Exp.(Å)	C.S (nm)	hkl	d_{hkl} Std.(Å)	Phase
Pure	26.5411	0.2054	3.3557	39.8	(110)	3.3498	SnO_2
	33.8356	0.2397	2.6471	34.7	(101)	2.6439	SnO_2
	37.9110	0.3082	2.3714	27.3	(200)	2.3686	SnO_2
	51.7123	0.2740	1.7663	32.2	(211)	1.7642	SnO_2
	54.7603	0.3425	1.6750	26.1	(220)	1.6749	SnO_2
	57.8082	0.5822	1.5937	15.6	(002)	1.5932	SnO_2
	61.8493	0.4452	1.4989	20.8	(130)	1.4981	SnO_2
	64.6918	0.3768	1.4397	25.0	(112)	1.4388	SnO_2
	65.9247	0.4795	1.4158	19.8	(301)	1.4149	SnO_2
	26.5412	0.2739	3.3557	29.8	(110)	3.3498	SnO_2
	30.4110	0.4109	2.9369	20.0	(222)	2.9214	In_2O_3
	33.8355	0.2397	2.6471	34.7	(101)	2.6439	SnO_2
	37.9113	0.3767	2.3714	22.3	(200)	2.3686	SnO_2
5%	50.7534	0.6164	1.7974	14.3	(440)	1.7890	In_2O_3
	51.7466	0.2740	1.7652	32.2	(211)	1.7642	SnO_2
	54.7603	0.4110	1.6750	21.8	(220)	1.6749	SnO_2
	57.6712	0.5480	1.5971	16.6	(002)	1.5932	SnO_2
	61.8836	0.7877	1.4982	11.8	(130)	1.4981	SnO_2
	64.7260	0.6164	1.4391	15.3	(112)	1.4388	SnO_2
	65.9932	0.4452	1.4145	21.3	(301)	1.4149	SnO_2
	26.5421	0.3767	3.3557	21.7	(110)	3.3498	SnO_2
	30.3767	0.4794	2.9402	17.2	(222)	2.9214	In_2O_3
	33.3219	0.3425	2.6867	24.2	(321)	2.7047	In_2O_3
	33.8377	0.3425	2.6471	24.3	(101)	2.6439	SnO_2
	37.1575	0.6849	2.4177	12.2	(330)	2.3853	In_2O_3
10%	37.9110	0.5480	2.3714	15.3	(200)	2.3686	SnO_2
	50.7877	0.4795	1.7962	18.3	(440)	1.7890	In_2O_3
	51.7808	0.3767	1.7641	23.5	(211)	1.7642	SnO_2
	54.7945	0.4452	1.6740	20.1	(220)	1.6749	SnO_2
	57.5000	0.5479	1.6015	16.5	(002)	1.5932	SnO_2
	61.9178	0.7877	1.4974	11.8	(310)	1.4981	SnO_2
	64.8288	0.4795	1.4370	19.6	(112)	1.4388	SnO_2
	65.9247	0.6507	1.4158	14.6	(301)	1.4149	SnO_2

equation), were shown in Table 1, which shows that the crystalline size decreases with the increasing of $\text{In}_2\text{O}_3/\text{SnO}_2$ ratio. The average crystalline size started from 26.8 nm, for the pure sample, and decreased to 21.8 nm using a 5% mix, then to 18.4 nm for the 10% mix ratio.

Figure 3 shows the AFM images for the $(\text{SnO}_2)_{1-x}(\text{In}_2\text{O}_3)_x$ thin films prepared using the PLD technique on glass slides at different mixing ratios, along with the associated granularity accumulation histograms. The pure SnO_2 sample has spherical shaped particles, and changed in their structure to a filamentous shape after doping with In_2O_3 . The diameters of these structures, which were calculated (using the Image-J software) as shown in Figure 4, decreased from 116 nm for the pure sample to, 90 nm for $x = 0.05$ and to 80 nm at $x = 0.1$.

Table 2 shows the average diameter and the root mean square surface roughness (RMS) for the $(\text{SnO}_2)_{1-x}(\text{In}_2\text{O}_3)_x$ thin films prepared at different ratios. The average particle diameter was found to decrease while the RMS roughness increased with increasing the mixing ratio due to the difference in growth mechanism. Such variations have previously been found to enhance gas sensor characteristics [8].

Figure 5 shows the transmittance spectra for the three $(\text{SnO}_2)_{1-x}(\text{In}_2\text{O}_3)_x$ thin film samples at different mixing ratios as annealed at 300 °C. The general feature for transmission spectra exponentially increases with the wavelength from 400 to 700 nm, while remaining essentially stable at larger wavelengths. All curves that appeared with vibrant shapes indicate regular deposition as mentioned by

Fig. 3. Three-dimensional AFM images and associated granularity distribution histograms for (a) SnO_2 (b) $(\text{SnO}_2)_{0.95}(\text{In}_2\text{O}_3)_{0.05}$ and (c) $(\text{SnO}_2)_{0.9}(\text{In}_2\text{O}_3)_{0.1}$ thin films prepared using the PLD technique.

Swanepoel [9]. The distances between successive vertices at two points depends on both the film thickness and the refractive index in those two points, so there is an obvious difference between the samples [10].

The energy gaps for the three samples were determined by extrapolating the straight-line portion of $(\alpha h\nu)^2$ with $h\nu$, as per the Tauc formula. The optical energy gaps were calculated as, $E_g = 2.9, 2.94$ and 2.96 eV for $x = 0, 0.05$ and 0.1 , respectively, which were essentially identical to the same calculated values reported in the literature [11]. The slight increment in bandgap by increasing the mixing ratio may be due to the decrease in crystalline size to the nano-scale that causes the quantum confinement effect [12] (see Fig. 6).

The results obtained from the Hall Effect measurements indicated that all films were n-type. The charge carriers concentration (n_H) and the major

charge carrier mobility (μ_H) were calculated at the different mixing ratios (x), as shown in Table 3. This table shows that the highest carrier concentrations appeared at $x = 0.10$, while the highest electron mobility (μ_H) appeared at a 5% mix concentration.

Fig. 7 shows the variation of $(\text{SnO}_2)_{0.9}(\text{In}_2\text{O}_3)_{0.1}$ gas sensitivity for 100 ppm NO_2 gas from 150°C to 300°C operating temperature. The gas sensitivity was found to increase with increasing temperature till 200°C , after that it decreased due to the variation of oxygen ion species adsorbed on the surfaces of metal oxide thin films; at low temperature, O_{ads}^- forms on the surface from ambient oxygen, and electrons extracted from sample, but at higher temperatures the dominant reaction $\text{O}_{\text{ads}}^- + e^- = 2\text{O}_{\text{ads}}$ which attracts an increased number of electrons from the sample when using clean air [13]. At the same time, a higher temperature can promote the oxygen ions desorption

Fig. 4. Calculation to determine rod diameter in the three samples (a) SnO_2 (b) $(\text{SnO}_2)_{0.95}(\text{In}_2\text{O}_3)_{0.05}$ and (c) $(\text{SnO}_2)_{0.9}(\text{In}_2\text{O}_3)_{0.1}$.

from SnO_2 , which decreases its gas responsivity [14]. The optimal working temperature of 200 °C is applied in the subsequent measurements.

Fig. 8 shows the variation of $(\text{SnO}_2)_{1-x}(\text{In}_2\text{O}_3)_x$ samples resistance, prepared at different ratios ($x = 0, 0.5, 0.1$ and 0.15), using different NO_2 concentrations, at 200 °C operating temperature. In all samples, the resistance was found to increase when the samples exposed to NO_2 gas. It seems that the sensitivity in the different samples varied according to surface

morphology and electrical properties, where the best samples appeared at $x = 0.1$ mixing ratio due to the small particle size and high charge carrier concentration of the associated sample. The gas sensitivity was found to increase with increasing gas concentration at a wide range of verity (from 10 ppm to 400 ppm).

Fig. 9 illustrates the variation of the four $(\text{SnO}_2)_{1-x}(\text{In}_2\text{O}_3)_x$ samples sensitivity against NO_2 gas concentrations, at 200 °C operating temperature. The sensitivity increased with nearly parabolic shape (has an R^2 values approach to 1 as shown in the Figure) with nearly stable at a high concentration. It is evident that the $(\text{SnO}_2)_{1-x}(\text{In}_2\text{O}_3)_x$ sample at $x = 0.1$ has the distinguish from others by high sensitivity characteristics. Increase the x ratio to 0.15 cause to reduce the gas sensitivity. Fig. 10 indicates this gas sensor stability when exposed to the same NO_2 concentration at 200 °C operating temperature.

Table 2

Average diameter and RMS roughness for $(\text{SnO}_2)_{1-x}(\text{In}_2\text{O}_3)_x$ thin films at different mixing ratios.

samples	Average Diameter (nm)	RMS roughness (nm)
Pure	85.11	14.5
5%	80.02	2.55
10%	77.54	5.61

Fig. 5. UV–visible transmission spectra for (a) SnO_2 (b) $(\text{SnO}_2)_{0.95}(\text{In}_2\text{O}_3)_{0.05}$ and (c) $(\text{SnO}_2)_{0.9}(\text{In}_2\text{O}_3)_{0.1}$ thin films.

Figure 11 illustrates the resistance variation behaviour with time when exposed to 100 ppm NO_2 gas, at 200 °C operating temperature. The response time (the time required to attain 90% of maximum increase to its stable value) was about 30 s, while the recovery time (the time required to get back to 10% of maximum increase) was about 40 s, for the optimum thin film gas

Table 3

Hall effect parameters for $(\text{SnO}_2)_{1-x}(\text{In}_2\text{O}_3)_x$ thin films at different ratios.

x	$\sigma_{\text{RT}} (\Omega^{-1} \cdot \text{cm}^{-1})$	$n \times 10^{18} (\text{cm}^{-3})$	type	$\mu_{\text{H}} (\text{cm}^2/\text{v} \cdot \text{sec})$
0.00	6.25	6.38	n	6.12
0.05	12.50	1.06	n	73.63
0.10	21.00	28.2	n	4.66

Fig. 6. Energy gap calculation using the Tauc formula for (a) SnO_2 (b) $(\text{SnO}_2)_{0.95}(\text{In}_2\text{O}_3)_{0.05}$ and (c) $(\text{SnO}_2)_{0.9}(\text{In}_2\text{O}_3)_{0.1}$ thin films.

Fig. 7. Sensitivity variation for $(\text{SnO}_2)_{0.9}(\text{In}_2\text{O}_3)_{0.1}$ against 100 ppm NO_2 gas with operating temperature.

Fig. 8. Resistance variation with time for $(\text{SnO}_2)_{1-x}(\text{In}_2\text{O}_3)_x$ thin films at different ratios (a) $x = 0$ (b) $x = 0.5$ (c) $x = 0.10$ and (d) $x = 0.15$, exposed to different NO_2 concentrations.

Fig. 9. Variation of NO₂ gas sensitivity against gas concentrations, at 200 °C operating temperature for (SnO₂)_{1-x}(In₂O₃)_x thin films prepared at different ratios (a) x = 0 (b) x = 0.5 and (c) x = 0.10 and (d) x = 0.15.

Fig. 10. Resistance variation with time for (SnO₂)_{0.9}(In₂O₃)_{0.1} thin films at different repetition, at same concentration (100 ppm) NO₂ gas, at 200 °C operating temperature.

Fig. 11. The resistance variation behaviour at 100 ppm NO₂ gas exposure, at 200 °C operating temperature for the (SnO₂)_{0.9}(In₂O₃)_{0.1} gas sensors.

sensor samples, which depend critically on the thin film microstructures [15].

4. Conclusions

NO₂ gas sensors were fabricated from SnO₂ and (SnO₂)_{1-x}(In₂O₃)_x at low cost. Structural measurements, surface morphology and electrical measurements showed a clear effect of the mix on the growth features of the nanoparticles, their crystalline structure and the charge carrier density which enhanced their use as gas sensor. The associated measurements confirmed this behaviour, as the sensitivity increased and the response and recovery times decreased when the doping ratio was 10%. From a temperature perspective, the best sensitivity appeared at an operating temperature of 200 °C. It can be used to measure NO₂ gas concentrations from 10 to 400 ppm with second order relation at high stability.

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