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Effect of ZnO Addition in Optical Properties of SnO_2-ZnO Nanoparticles as Sulfide Gas Sensor

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ABSTRACT
Thin film of SnO_2 and SnO_2–ZnO were synthesized with chemical liquid deposition method, and characterized by UV/VIS/NIR-Spectrophotometer, FTIR, SEM, TEM and XRD. Characterization studies showed SnO_2 nanoparticle size from the range 38 – 71 nm of diameters, and SnO_2-ZnO showed the range 25 – 85 nm of diameters. Optical properties between two different of sensor showed on the analyses results of thickness. Application the sensor on the gas detection also showed different response of wavelength shifting of the reflectance in the near infrared range.
Keywords: metal oxide, SnO_2-ZnO, sulfide gas sensor, UV/VIS/NIR-Spectrophotometer

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I. INTRODUCTION

Nanoparticle synthesis and its application as nanosensor is spreading more recently because increasing the needs of pollution detection. SnO_2 as examples of nanoparticles which can be used as gas sensor [1] has specific character, and an interest of research has been shifted to thin film sensors due to small size, low cost production, low energy consumption and possibility of integration with electronics and modified with other nanoparticle compounds for getting better sensitivity and selectivity. Optical properties as one part of nanoparticle character can be modified and analyzed during synthesis process. Information for a thin film could be obtained from transmittance spectrum by spectrophotometer UV/VIS. Envelope method could be applicable for film thickness determination which is used to produce homogen thickness of sensors [2]. The thickness were calculated from interferences of transmittance spectrum in the ultraviolet-visible regions. In this research, ZnO was added to modify the characterization of gas sensor.

II. EXPERIMENTAL DESIGNS

Thin film of SnO_2 and SnO_2-ZnO can be produced by deposition of this metal oxide on the glass substrate. Soda lime float glass with 1 – 1.2 mm of thickness (YanchengHuida Medical Instruments Co.) was used in this experiment. The substrate was cleaned by rinsing into 40°C of acetone for 15 minutes, then rinsed with ethanol at room temperature, final washed with distilled water and dried. $SnCl_2.2H_2O$, $ZnCl_2$, and NaOH were used as the precursors, and deposition was done by spraying. Annealing temperature was varied from 200 ºC - 500ºC. Thin film of SnO_2-ZnO sensor was synthesized by simple method of chemical liquid deposition with molarity ratio of 1:0.25, and characterized using UV/VIS/NIR-Spectrophotometer (Shimadzu UV 3101 PC) at λ = 200 – 2400 nm, FTIR Spectrophotometer, Optic and Scanning Electron Microscope, and also XRD with Cu[(Kα)] with $\lambda\alpha_1$ = 1.54060 nm and $\lambda\alpha_2$ = 1.54439 nm. Application of sensor to the sulphide gas using CS_2 cylinder gas standard, which was flowed to the closed chamber of sensor thin film, with flow regulator to fulfil 20 ppm content of gas in chamber with the response time of 2 minutes.

III. EXPERIMENTAL RESULTS

3.1 FTIR Spectroscopy

Infrared spectrum of SnO_2 and SnO_2-ZnOnano thin film showed specific peaks for annealing temperature variation from 200 ºC to 500 ºC. It was analized by FTIR in the range from 400 to 4500 cm^{-1}. The bands between 400-800 cm^{-1} correlated to metal oxide bond (SnO_2 and SnO_2-ZnO). Bands around 800 – 1700 are due to the oxygen stretching and bending frequency.Infrared spectrum of SnO_2nano thin film showed specific peaks at 3425 cm^{-1}, 1625 cm^{-1}, and 615 cm^{-1} for annealing temperature 500 ºC, and was not showed the peak around 1600 for the SnO_2-ZnO. It can be seen from the spectrum that the highest annealing temperature showed results as the most clear spectrum. Functional group –OH seems wider at the lower annealing temperature, showed at band around 3400 cm^{-1}.

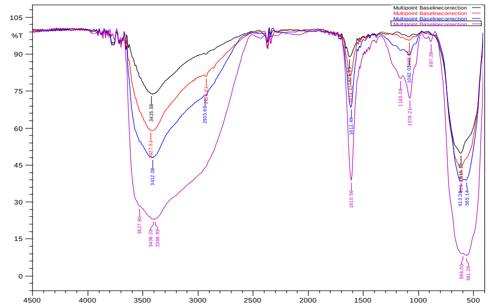


Fig.1 Infrared spectrum of SnO_2nano thin film variance annealing temperature 200 °C (purple), 300 °C (blue), 400 °C (red), and 500 °C (black)

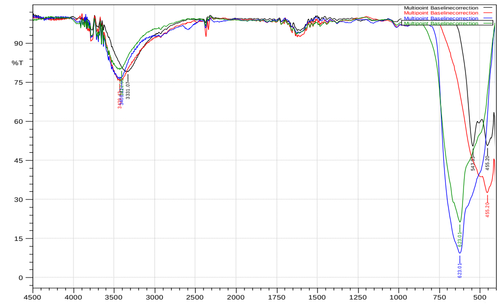


Fig.2 Infrared spectrum of SnO_2–ZnO (1:0.25) nano thin film variance annealing temperature 200 °C (blue), 300 °C (green), 400 °C (red), and 500 °C (black)

3.2 UV/VIS Spectroscopy

Optical measurement of SnO_2-ZnO nanoparticle was carried out with UV/VIS-spectrophotometer, and analysis result showed increasing of annealing temperature can decrease the transmittance or increase absorbance. The results is average spectrum of 10 times measurement in each annealing temperature, and done in the room temperature with the glass substrate slide as the standard.

The thickness of the film was calculated using the equation [5]:

$$\mathbf{t} = \frac{\lambda_1\lambda_2}{2(\lambda_1 n_2 - \lambda_2 n_1)}$$

where n_1 and n_2 are the refractive indices corresponding to the wavelengths λ_1 and λ_2. The refractive indices n at various wavelength were calculated using the envelope curve for T_{max} (T_M) and T_{min} (T_m) in the transmission of UV/VIS spectra as given below:

$$\mathbf{n} = \left[N + (N^2 - N_s^2)^{1/2}\right]^{1/2}$$

where:

$$N = 2n_s\frac{T_M - T_m}{T_M T_m} + \frac{n_s^2 + 1}{2}$$

And n_s is the refractive index of the substrate (n_s = 1.52 for glass).

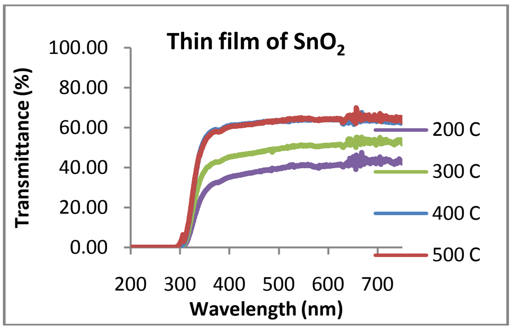


Fig.3UV/VIS spectrum of SnO_2nano thin film

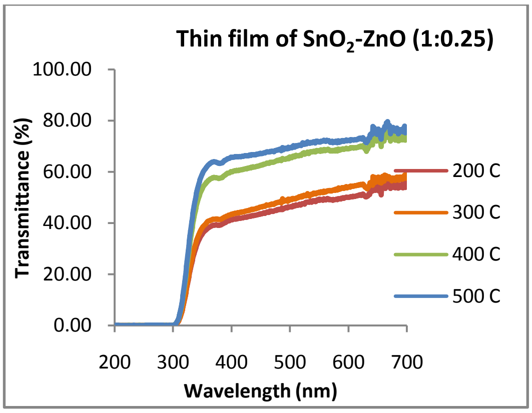


Fig.4UV/VIS spectrum of SnO_2-ZnO nano thin film

The results of thickness analyses by envelope method for SnO_2 thin film are below:

Table 1.Thickness of SnO_2 at annealing temperature 200 °C

λ (nm)	**T_{MAX} (%)**	**T_{min} (%)**	**Thickness (nm)**
796	66.84	66.79	
701	66.76	66.39	729.33
632	66.69	66.06	908.68
577	66.63	65.77	977.17
527	66.57	65.48	796.72
471	66.50	65.12	255.05
		Average	733.39

Table 2. Thickness of SnO_2 at annealing temperature 300 °C

λ (nm)	**T_{MAX} (%)**	**T_{min} (%)**	**Thickness (nm)**
796	69.00	67.00	
701	68.34	66.40	730.37
632	67.81	65.92	910.20
577	67.34	65.49	979.08
527	66.87	65.07	798.78
471	66.30	64.54	256.80
		Average	735.05

Table 3. Thickness of SnO_2 at annealing temperature 400 °C

λ (nm)	T_{MAX} (%)	T_{min} (%)	Thickness (nm)
796	59.36	54.63	
701	57.35	53.65	735.11
632	55.71	52.85	917.61
577	54.27	52.14	988.89
527	52.83	51.44	809.81
471	51.05	50.57	266.68
		Average	743.62

Table 4. Thickness of SnO_2 at annealing temperature 500 °C

λ (nm)	T_{MAX} (%)	T_{min} (%)	Thickness (nm)
796	45.39	41.80	
701	42.61	40.02	737.43
632	40.35	38.56	923.22
577	38.36	37.29	998.32
527	36.37	36.01	822.55
471	33.92	34.44	280.41
		Average	752.39

Table 5. Thickness of SnO_2-ZnO at annealing temperature 200 °C

λ (nm)	T_{MAX} (%)	T_{min} (%)	Thickness (nm)
796	65.51	63.06	
701	64.46	60.67	715.61
632	63.60	58.72	890.94
577	62.85	57.01	956.20
527	62.10	55.31	774.99
471	61.17	53.19	236.96
		Average	714.94

Table 6. Thickness of SnO_2-ZnO at annealing temperature 300 °C

λ (nm)	T_{MAX} (%)	T_{min} (%)	Thickness (nm)
796	63.39	64.75	
701	61.49	60.21	708.47
632	59.94	56.51	877.94
577	58.58	53.26	937.01
527	57.22	50.02	751.29
471	55.55	46.01	213.42
		Average	697.62

Table 7. Thickness of SnO_2-ZnO at annealing temperature 400 °C

λ (nm)	T_{MAX} (%)	T_{min} (%)	Thickness (nm)
796	78.40	77.27	
701	76.35	74.62	726.87
632	74.68	72.45	905.29
577	73.21	70.55	972.96
527	71.75	68.65	792.16
471	69.94	66.31	251.07
		Average	729.67

Table 8. Thickness of SnO_2-ZnO at annealing temperature 500 °C

λ (nm)	T_{MAX} (%)	T_{min} (%)	Thickness (nm)
796	79.13	77.08	
701	76.80	74.85	730.53
632	74.90	73.04	910.36
577	73.23	71.44	979.23
527	71.56	69.86	798.90
471	69.50	67.89	256.87
		Average	735.18

3.3 XRD Spectroscopy

XRD pattern of SnO_2 variance 500 ºC were calculated based on Bragg law,

$$n\lambda = 2d \sin \theta$$

whereλ is X-ray wavelength, d is the distance between lattice planes, θ is the angle of incidence with lattice plane, and n is integer [3,4].

Quantitative information concerning of preferential crystallite orientation was obtained from another texture coefficient TC (*hkl*) defined as [5]:

$$TC(hkl) = \frac{\frac{I(hkl)}{I_0(hkl)}}{\sum_n \frac{I(hkl)}{I_0(hkl)}} \times 100\%$$

where I (hkl) is the measured relative intensity of a plane (hkl) and I_0(hkl) is the standard intensity of the plane (hkl).Observed peaks of XRD pattern in the Figure 5, are indexed assuming SnO_2 phase, giving peaks position, with Miller indices (110), (101), (200), (211), (220), (310) and (301) planes.

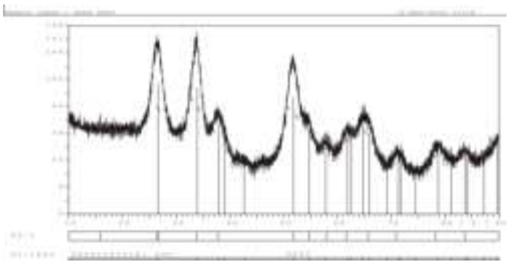


Fig. 5XRD spectrum of SnO_2nano thin film

Observed peaks of XRD pattern in the Figure 5, are indexed assuming SnO_2–ZnO phase, giving peaks position, with Miller indices (110), (100), (101), (200), (211), (002), (220), (310) and (301) planes.

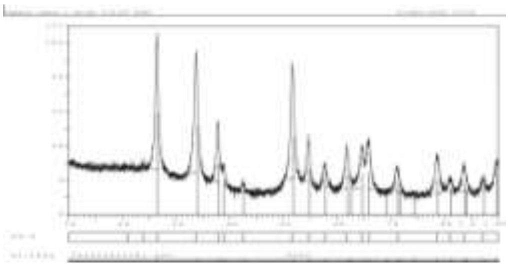
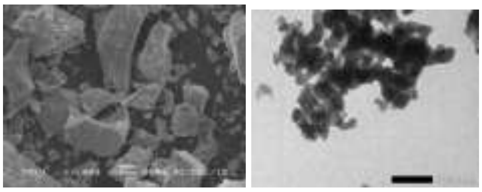


Fig. 6XRD spectrum of SnO_2–ZnOnano thin film

3.4 Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM)

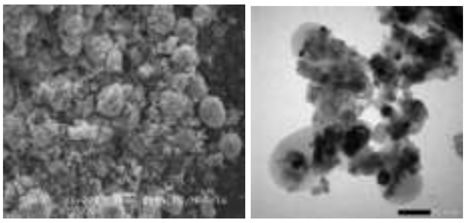
Characterization studies by SEM showed SnO_2 with maximum annealing temperature 500 °C has nanoparticle size from the range 38 – 71 nm of diameters.



(b)

Fig. 7 (a) SEM analysis result and (b) TEM analysis result of SnO_2nano thin film

Characterization studies by SEM showed SnO_2–ZnO with maximum annealing temperature 500°C has nanoparticle size from the range 25 nm – 85 nm of diameters.



(a) (b)

Fig. 8 (a) SEM analysis result and (b) TEM analysis result of SnO_2–ZnOnano thin film

3.5 Application of SnO_2 and SnO_2-ZnO nano Thin Film to CS_2 Standard

Application of SnO_2thin film for CS_2 gas sensor were tested using UV/VIS/NIR-spectrophotometer showed shifting of % Reflectance peak from wavelength 1274 cm^{-1} with 45.21 % of reflectance to wavelength 1428 cm^{-1} with 79.21%. This response as starting point for detecting gas quantitavely at wavelength 1428 cm^{-1}. Application of SnO_2–ZnOthin film for CS_2 gas sensor were tested also using UV/VIS/NIR-spectrophotometer showed shifting of % Reflectance peak from wavelength 1516 cm^{-1} with 72.01 % of reflectance to wavelength 1520 cm^{-1} with 81.63%. This response as starting point for detecting gas quantitavely at wavelength 1520 cm^{-1}. The research will be continued with statistical approach of quantitative analysis by making standard curve and determination of detection limit.

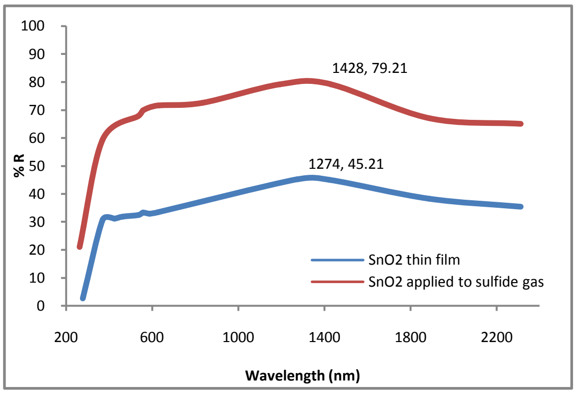


Fig. 9 Application of SnO_2 to sense 20 ppm of CS_2 gas standard

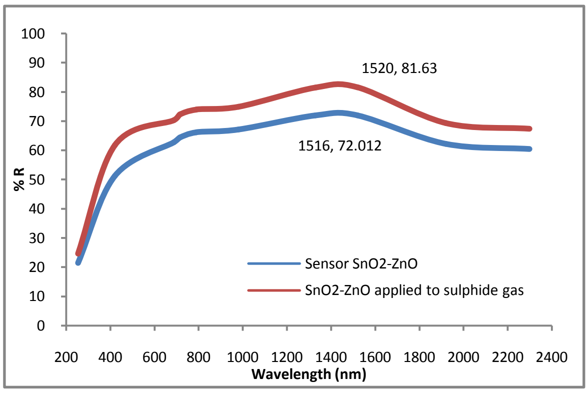


Fig. 10 Application of SnO_2–ZnO to sense 20 ppm of CS_2 gas standard

CONCLUSION

SnO_2 and SnO_2-ZnO nanoparticles can be produced by simple chemical liquid deposition, and at annealing temperature of 500 ºC can get particle size from the range 38 – 71 nm of diameters for the SnO_2, and 25 nm – 85 nm of diameters for SnO_2-ZnO. The optical properties of thin film showed on thickness, SnO_2 733.39 – 752.39 nm, and for SnO_2-ZnO on the range 697.62 – 735.18 nm. The comparison in application of gas sensor to sulphide gas showed different response, SnO_2thin film for CS_2 gas sensor were tested using UV/VIS/NIR-spectrophotometer showed shifting from wavelength 1274 cm^{-1} with 45.21 % of reflectance to wavelength 1428 cm^{-1} with 79.21%. This response as starting point for detecting gas quantitavely at wavelength 1428 cm^{-1}. Application of SnO_2–ZnOthin film for CS_2 gas sensor were tested also using UV/VIS/NIR-spectrophotometer showed shifting of % Reflectance peak from wavelength 1516 cm^{-1} with 72.01 % of reflectance to wavelength 1520 cm^{-1} with 81.63%.

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