PREPARATION AND CHARACTERIZATION OF ZnO: SnO_2 NANOCOMPOSITE THIN FILMS ON POROUS SILICON AS H_2S GAS SENSOR

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Mixed nanocomposite thin films of ZnO-SnO_2 were prepared by chemical spray pyrolysis. It deposited on glass and porous silicon substrates at 400 C°. The structure properties of the sensor material were analyzed by XRD and AFM. The results obtained that the films are polycrystalline with nano grain size. the optical transmission was decreased while the optical energy gap was increased with increasing of SnO_2 ratio. The sensor response was estimated by changing in the electrical resistance of the sensor films with 25% H_2S gas of different temperatures. The mixed oxide sensor gives a sensitivity of H_2S gas three times greater than the sensitivity of a single SnO_2 gas sensor. The higher sensitivity of mixed oxide is 92% on porous silicon at 200C° operating temperature ,with response time of 16s and recovery time 28s. The high response of ZnO-SnO_2 nanocomposite sensor is an indicator of a high efficiency of H_2S gas sensing.

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1. Introduction

Metal oxide semiconductor were used as gas sensing materials for detecting of oxidizing and reducing gases. Many efforts have been focused on improving metal oxide selectivity by doping it with elements or other metal oxides such as Ag doped SnO_2 [1], Mg doped ZnO [2], CuO doped SnO_2 [3], and ZnO doped SnO_2 [4]. Also, mixed oxides thin films can be used to give a good gas sensor sensitivity and selectivity, especially when it has a nano particle size and different work functions, due to the increasing of gases adsorption on the oxide surface [5-8]. The mixed films of ZnO-SnO_2 have better sensor characteristics than pure SnO_2 or ZnO, because of the porosity that created by ZnO into SnO_2 matrix [9-13]. Karthic et al [14] found that porous silicon improves the gas sensitivity of ZnO-SnO_2 for CO_2 gas by a factor of 2 with respect to single oxide. H_2S is a highly toxic gas and its detection is very important, so it is necessary to find an excellent gas sensor to detect it. Especially at its low concentration as reported in many studies in the literature [15-18]. In this study a mixed ZnO-SnO_2 nanocomposite deposited on glass and porous silicon by chemical spray pyrolysis, then its structural properties, optical properties and sensing characteristics of H_2S detection have been investigated

2. Experimental details

ZnO-SnO_2 nano composite thin films were deposited on glass and porous silicon slides by chemical spray pyrolysis at 400C°. Glass substrate were cleaned with detergent water in ultrasonic bath then dipped in acetone for five minutes. Porous silicon layers were formed on p-type (111) oriented by electrochemical method with 40mA current and time of 20 minutes. ZnO and SnO_2 pure and mixed thin films prepared by using 0.1M aqueous solutions of $ZnCl_2.2H_2O$ and SnCl2.H_2O. The ratio of mixed films were 20 and 60 vol% of SnO2 solution. The spraying time

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period was 5s followed by 30s wait intervals. The deposition rate is 2 ml/min. structural characteristics were examined by XRD (Shimadzu 6000PW 1050 A˚ Target: Cu-kα, Scan mode: continuous scan, Current: 30 mA , Voltage: 40 kV ,Wavelength 1.5406 A). AFM (AA3000) is used to identify the film topography. The optical transmission and optical absorption were measured using uv-vis spectrophotometer type (sp-8001) in the wavelength range 300-1100nm .The gas sensing characteristics of deposited thin films were evaluated by measuring the change in electrical resistivity toward 25% H2S gas, at different operating temperatures.

3. Results and discussion

3.1. Structural analysis

The XRD patterns of the ZnO-SnO_2 nanocomposites on the glass and porous silicon are presented in figure1. It is evident that the structure is polycrystalline. This structure has many peaks of hexagonal ZnO (JCPDS no. 13-0311) and many phases of tetragonal SnO_2 which are Sn_2O_3 and Sn_3O_4 (JCPDS no.29-1484). The mixed films at ratio 20 vol% SnO_2 (ZS3) does not appear as a compound of ZnO and SnO_2, so the structure is a composite. While at ratio 60 vol % SnO_2 (ZS5) there is a compound of Zn_2SnO_2 in the direction (531). The crystal size of the preferred ZnO (002) peak is equal to 17.68nm on the glass slide and 41.65nm on the porous silicon slide.

The atomic force microscopy (AFM) is used to study the form of thin films surface which an important factor for the gas sensor applications. The interaction of gases with the surface depend on particle size and surface roughness [18]. AFM images of ZS3 and ZS5 films on glass substrates are showing in Fig (2-a, b) which have a high homogeneous and regular granular distribution. The average grain size these films are 63.23nm and 108nm respectively and have RMS of 1.01nm for ZS3 and 1.28nm for ZS5. Also they have average roughness of 0.852nm and 1.1nm respectively. The increase in the grain size with increasing of the mixed ratio may be related to the forming of compound structure as well as composite structure.

The deposition of metal oxide on porous silicon improves the properties of the sensor by increasing oxygen adsorption. Fig. 3 c-d shows AFM images of the ZS3 and ZS5 films on porous silicon which gives the average grain size of 70.57nm and 85.53nm respectively. While the RMS and average roughness were decreased compared with thin films deposited on glass substrate.

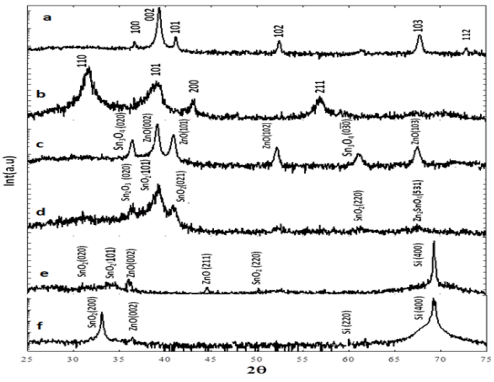

Fig. 1. XRD patterns for Mixed ZnO- SnO_2 thin films (a): ZnO (b): SnO_2 (c):ZS3/glass (d):ZS5/glass (e):ZS3/PS (f):ZS5/PS.

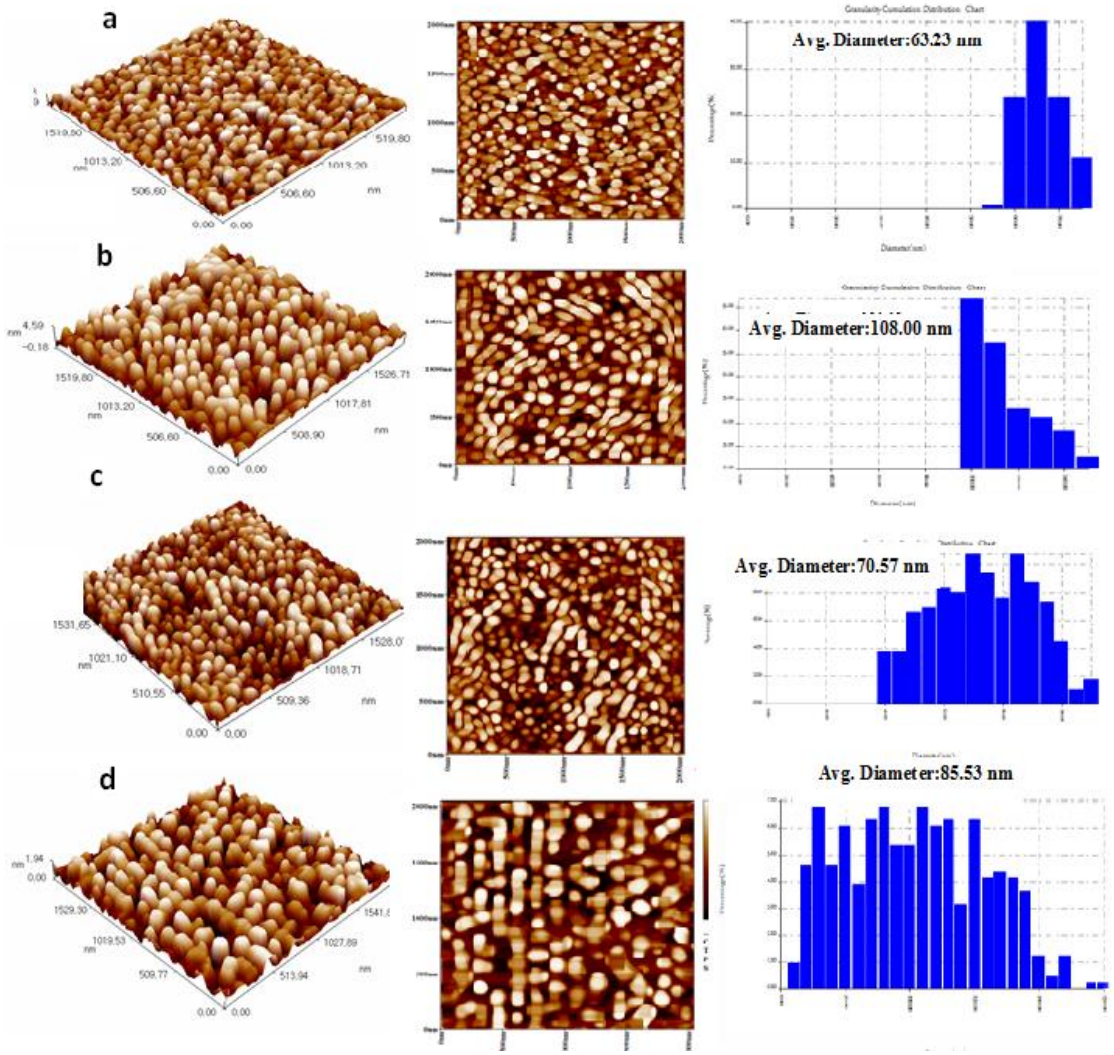

Fig. 2. AFM images of mixed ZnO- SnO_2 thin films (a):ZS3/glass (b):ZS5/glass (c):ZS3/PS (d):ZS5/PS.

3. Optical properties

The optical transmission of pure and mixed ZnO with SnO_2 thin films were obtained in Fig. 3. From this figure the value of pure ZnO transmission at 750nm wave length is 81%, while at mixed thin films it is decreased with the increasing ratio of SnO_2. This may be related to the oxygen vacancies due to SnO_2 increases because the mixed of two oxides are made changes on the film structure and the surface nature as shown in the AFM image. The film roughness increases the optical scattering that lead to decreasing the optical transmission, this behavior agreed with D.Chakraborty et al. [19] results.

The plot of $(\alpha h\upsilon)^2$ versus $(h\upsilon)$ of the prepared films are shown in Fig. 4. The optical band gap values are evaluated from this figure as shown in table 1. The value of ZnO energy gap is equal to 3.1 eV., which agree with Saad khafory et al [20] results and the value of SnO_2 energy gap is equal to 3.5 eV while the value of the mixed films are between these two values. The increase of E_g with increasing SnO_2 ratio may be due to the Burstein mass effect [21]. These results are agreed with the findings by Tharsika et al [7].

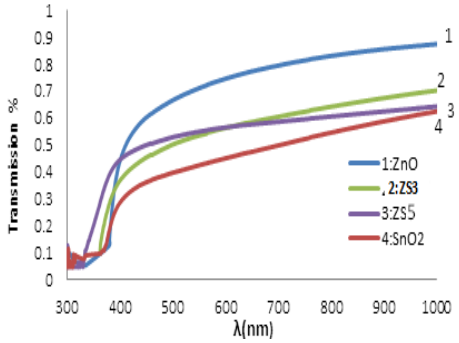

Fig. 3. Optical transmission for pure and mixed of ZnO-SnO_2 thin films.

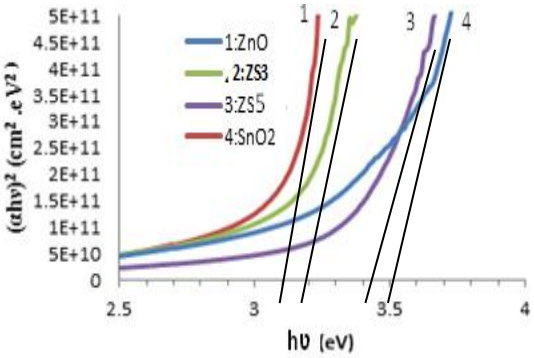

Fig. 4. Optical energy gap of pure and mixed ZnO-SnO_2thin films.

Table 1. The value of Eg for prepared thin films on glass substrate.

Sample	Energy gap(eV)
ZnO	3.10
ZS3	3.19
ZS5	3.43
SnO_2	3.5

4. Gas sensing characteristics

The sensitivity of metal oxide gas sensor depend on many factors, such as type of the oxide, substrate temperature, crystal structure, grain size, the morphology and porosity surface. From these factors the substrate temperature is an important factor which effects on the gas interaction with the oxide according to the dynamic process. The oxygen of the air bonded by vacancies on the oxide surface, which oxidized that surface and increases its resistance as the following equations [22]:

$$O_{2(gas)} \rightleftharpoons O_{2(ads)} \quad (1)$$

$$O_2 + e^- \rightleftharpoons {}^-O_{2(ads)} \quad (2)$$

$$O_{2(ads)} + e^- \rightleftharpoons 2{}^-O_{(ads)} \quad (3)$$

$$O_{(ads)} + e^- \rightleftharpoons O^{-2}{}_{(ads)} \quad (4)$$

Fig. 5 (a, b) obtain the change of relative sensitivity with time for H_2S at 25% concertation with mixed oxide surface deposited on glass substrates. The sensitivity calculated according the following relation:

$$S = \frac{Rg-Ra}{Rg} * 100\%.$$

where: Rg: gas resistance, and Ra: air resistance.

The response time (t_{res}) and recovery time (t_{rec}) were evaluated for different thin films and at different substrate temperatures from figure 5. The sensitivity increased when the sensor exposed to H_2S to maximum value then it decreased to a value approach to the initial when H_2S gas got out. The composite ZS3 thin films, which has the best structural and optical properties, give 46% sensitivity with t_{res} 12s and 19s t_{rec} at RT. Also, it gives sensitivity of 59% at 100C° operation temperature with 15s t_{res} and 30s for t_{rec}, this sensitivity value is greater than the sensitivity of pure SnO_2 thin films, moreover its operating temperature is 100C° instead of 200C°. At 200C° operating temperature the value of S% for mixed thin films was decreased to 36% with 11s t_{res} and 15s t_{rec}. This decreasing of the sensitivity is related to the high desorption of H_2S gas. The sensitivity is increased to 48% with the increasing of mixing ratio to 60% SnO_2 (ZS5), with 9s t_{res} and 15s for t_{rec} at R.T. Then the sensitivity increased to 55% at 100C° with 9s t_{res} and 13s t_{rec} .in addition, the S% arrives to 83% at 200C° operating temperature with 15s t_{res} and 17s t_{rec}. This improvement of the sensitivity means H_2S was interact with the grains of the surface as well as with adsorbed oxygen, so the dissociation gas was happening on the surface according to the equations [23].

$$7H_2S + 3SnO_2 \rightleftharpoons 3SnS + 4SO_2 + 7H_2O \quad (5)$$

$$7H_2S + 3ZnO \rightleftharpoons 3ZnS + 4SO_2 + 7H_2O \quad (6)$$

The composite of ZnO and SnO_2 is characterized as heterojunction of n-n according to the optical results. This composite has a nano grain size and a high porosity as shown in the AFM analysis. The n-n heterojunction contact gives a high electric concentration which is increased the oxygen adsorption on the surface. These parameters approved that the prepared mixed oxide gives a high sensitive characterization towards H_2S which is three times greater than single oxide films at RT. These results agree with Plobmondel et al. [24] results.

Fig. 5 (c, d) obtain the sensitivity of (ZS3) and (ZS5) with time in different temperatures deposited on porous silicon toward 25% H2S gas. The value of S% increased from 25% at RT to 57% at 200C°, while the response time decreased from 12s to 6s at the same interval and the recovery time decreased from 15s to 14s. The sensitivity of the (ZS5) on porous silicon increased from 46% at RT to 92% at 200C°,while t_{res} increased from 12s to 16s and t_{rec} increased from 12s to 30s at the same temperature interval. The increasing in the sensitivity related to the effect of the porous silicon. That porous silicon gives a high surface area, which enhance oxygen adsorption that lead to increase the sensing response [7]. Also, the interaction of H_2S happens in bulk films as well as on the oxide surface. The sensing materials with low dimensional structures have a large surface area, which could provide more adsorption sites, for the oxygen species and the tested gases. Also it facilitates the interaction between the oxide surfaces and gas molecules [25].

For the deposited films on the porous silicon. There is more material deposited within the porous which contributes in an increase of sensing response while the gas takes more time to desorb from the porous. For this reason the recovery time was increased as shown in Fig. 5. Also, the higher value of sensitivity on porous silicon may attributed to the formation of p-n heterojunction between PS and n-type of metal oxides. This increases the concertation charge carriers, and it makes the oxide surface relatively more adsorptive to give high sensitivity at lower temperature [7], as shown in Fig. 5.

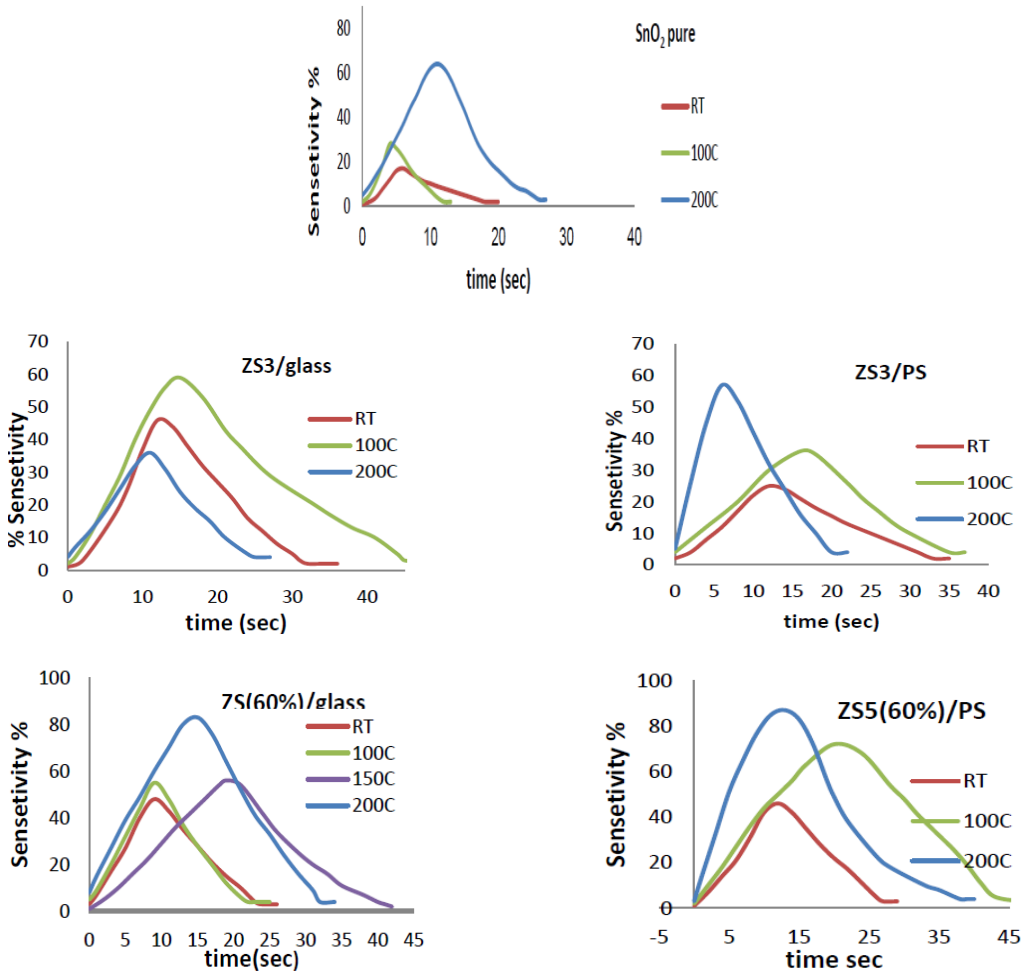

Fig. 5. The sensitivity of ZS3, ZS5 films on glass and porous silicon at different temperatures.

3. Conclusions

Nanocomposite ZnO-SnO_2 thin films deposited on glass and porous silicon slides were tested for sensing applications. XRD and AFM technique obtained that a polycrystalline with nano grain size were prepared. The films have high optical transmission with direct energy gap and their depended on the mixed ratio of SnO_2.The films have high sensing characteristics toward 25% H_2S to give a sensitivity of 46% on glass at RT which is greater than pure SnO_2 by three times. Also the sensor gives a high sensitivity on the porous silicon up to 92% at 200C° .The modulation of depletion region at n-n heterojunction between ZnO-SnO_2 and at p-n heterojunction between ps and metal oxides enhanced the activity of adsorption for oxygen and H_2S gases. This has clearly increased the sensor response characteristics.

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