Tin Dioxide Nanostructure Gas Sensor for Acetone and Methanol Detection

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Articleinfo

Received
13/4/2016
Accepted
8/5/2016

Keywords:
Nanostructure, gas sensor, screens print, thick films, simple evaporation.

ABSTRACT

Simple and efficient technique were successfully used to prepare Tin dioxide (SnO_2) nanostructure by simple evaporation method, using single stage horizontal tube furnace under atmosphere pressure and quartz tube with Argon flow without additive. SnO_2 thick films were synthesized using simple, homemade, low-cost efficient screen print technique. The thick films were heated at 500 ^{0}C for one hour to vanish the organic material and any residual impurities. The prepared thick films were investigated using different techniques and apparatus, X-Ray and FESEM to study the structural and morphology of the films, the X-ray results show that the films are polycrystalline with sharp and high intensity peaks indicating high crystalinity of the product. The FESEM Images show homogenous nanostructure with high porosity the dimension range 40-70 nm, optical properties was studied with photoluminescence emission (PL) and transmittance in UV-Visible range. SnO_2 sensor was built up by electroding the thick films and used for Acetone and methanol detection.

الخلاصة

تقنية غير معقدة وكفوءة تم استخدامها بنجاح لتحضير **(SnO_2)** بتراكيب نانوية وذلك باستخدام تقنية التبخير البسيط باستخدام فرن انبوبي وانبوبة كوارتز وبوجود غاز الاركون وضمن الضغط الجوي بدون وجود عامل مساعد . تم تصنيع اغشية سميكة من **(SnO_2)** باستخدام تقنية الطباعة على الشبكة وهي بسيطة وذات كلفة واطئة وفعالة، ان هذه الطريقة تعطينا اي تصميم او ابعاد للغشاء وبالتصاقية جيدة بين الغشاء والقاعدة. بعد ذلك تم تسخين الاغشية المحضرة لمدة ساعة وعند درجة حرارة 500 م للتخلص من الرابط العضوي واي شوائب اخرى. تم دراسة الخصائص التركيبية و دراسة السطح للاغشية المحضرة بفحصها ب باجهزة ال X-ray, FESEM حيث اظهرت فحوصات الحيود بالاشعة السينية ان الاغشية ذات تركيب متعدد التبلور مع قمم حادة ذات شدة عالية مما يدل على تبلور جيد للمادة، واظهرت صور المجهر الالكتروني الماسح تراكيب نانوية بابعاد تتراوح 40-70 نانومتر .وتم دراسة اخصائص البصرية للاغشية المحضرة من خلال فحص التألقية الضيائية (PL), كذلك قياس النفوذية وفجوة الطاقة. تم بناء االمتحسس االغازي بعد تقطيب الاغشية وبنفس تقنية الطباعة على الشبكة وتم استخدامه للكشف عن الاسيتون والميثانول.

INTRODUCTION

Evolution of methods for the controlled fabrication of nanostructures is currently the super goal in the domain of nanoscience and nanotechnology. Newly, much interest has been pointed to the use of low dimensional nanostructures such as nanoparticles, nanowires (NWs), and nanotubes, as building blocks in the production of hierarchical nanostructures because of different novel applications [1, 2, 3]. Researchers and scientists developed a techniques and methods to produce a wide range of different nanostructures. Hierarchical nanostructures based on NWs can be used as solar-cells, optoelectronic devices and gas sensors [5, 6, 7]. Due to characteristic high porosity of hierarchical nanostructures.

Precise detection of acetone and methanol scales in expel human breath, helping as breath indications for some diseases such as diabetes and mouth bad smell, may give useful information for early diagnosis of these diseases and environmental hazard. Using semiconductor metal oxide (SMO) gas sensors have attracted much attention due to low cost fabrication, miniaturization, and integration into portable devices [8, 9].

SnO_2 is an important semiconductor with a wide band gap. It has latent qualities can be utilized in many applications and manufacturing optoelectronic devices such as gas sensors, photodetectors and solar cells. It's one of the important semiconductors that have been widely used for gas sensors. Since nanostructures such as nanowires, nanotubes, nanorods and nanoparticles have high surface to volume ratio [10, 11, 12], synthesis of these morphologies become the goal of researchers [13]. Recently, SnO_2 nanostructures have been synthesized by different methods such chemical method, hydrothermal processing, thermal evaporation, spray pyrolysis and oxidation technique. In this work, SnO_2 nanostructures synthesized successfully by the simple thermal reduction method with flow of argon and the product were investigated.

MATERIALS AND METHODS

In simple thermal reduction synthesis method, a 80 cm long quartz tube with an inner diameter of 3 cm open on both sides one for Ar gas inlet and the other as excused was mounted inside a horizontal tube furnace. 99.99 % pure Sn powders were placed in an alumina boat (1 × 1× 10 cm^3) positioned at the center of the quartz tube while pre cleaned Si substrate was placed in front of the boat,

the quartz tube was purged several times. The temperature in the tube furnace was rapidly raised up to 800 ^{0}C kept for 1 hour during the process, a steady flow of Ar gas (99.99 %) at a rate of 50 sccm was continued. The process continues for one hour then the furnace turn off to cool down. White powder was appears on the alumina boat and on the Si substrate. The product was collected carefully then thick films were made using efficient low coast screen print method, thick films were deposited on different substrates (Glass and p-type Si) the thickness was ranging between (3-4µm) to be characterized with different apparatus, the structural properties and morphology of the films by x-ray diffraction (XRD) using (***miniflex II Rigaku, Japan***) Cu Kα radiation, field emission scanning electron microscopy (FESEM) (***Hitachi-S 4160***-Japan), optical properties and transmission measurements were carried out using a UV/visible spectrophotometer ***Optima Sp-3000 plus UV-Vis-NIR (Split- beam Optics, Dual detectors)***in a range between 300 and 900nm. The PL spectra at room temperatures were achieved from 320 to 600nm using (**Perkin Elmer *Spectrophotometer Luminescence LS 55 equipped with FL Win lab software***) with excitation wave length 280nm from Xenon lamp.

To build the detector, a silver (IED) electrode was deposited on some of these films by screen print method. The sensing measurements were done using a homemade gas sensing system of 5000cm^3 chamber.

RESULTS AND DISCUSSION

The thick films were examined by (XRD) diffraction to study structural properties of the prepared films, Figure 1 shows polycrystalline structure with sharp peaks indicate high crystallinity, all the diffraction peaks refers to a rutile phase of SnO_2 according to JCPDS Card no. 411-445, (110), (101), (210), (211), no other peaks appears indicating high purity of the screen printed films. It's obvious from diffraction pattern the dominated growth with (110) plane. The crystallite size and structural parameters of the SiO_2 rutile phase estimated using Equations 1 and 2 [14, 15] respectively and extracted in Table 1:

$$D = \frac{0.9\lambda}{\beta cos\theta} \quad (1)$$

Where D: crystallite size , λ= 1.5406 A˚, β: the FWHM and θ: the diffraction angle.

$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \quad (2)$$

Table 1: Structural properties estimated from (XRD) pattern.

(hkl)	D (nm)	a, b (nm)	c (nm)
(110)	38	4.691	3.174
(101)	34	-	-
(210)	33	-	-

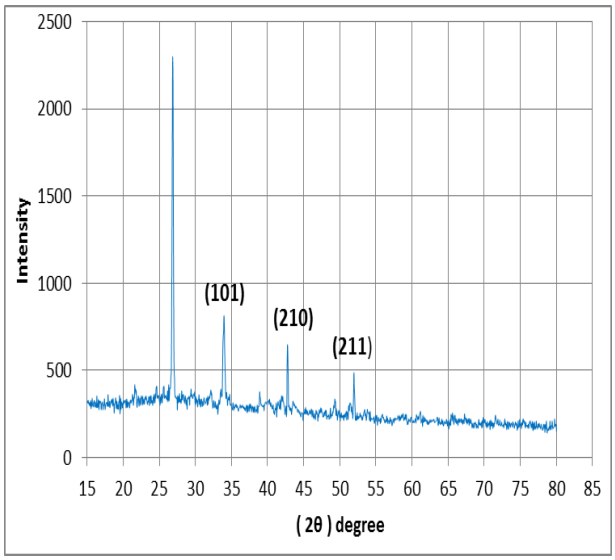
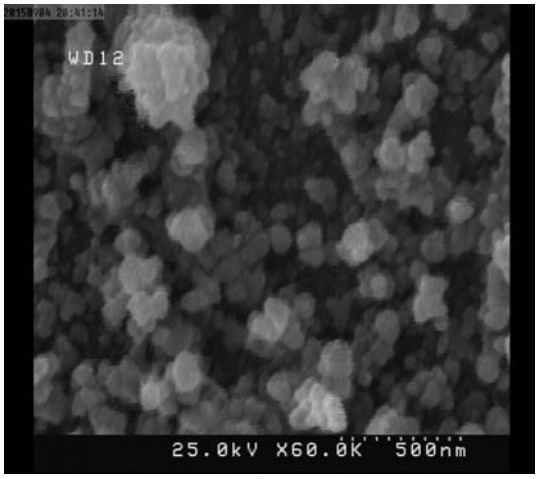


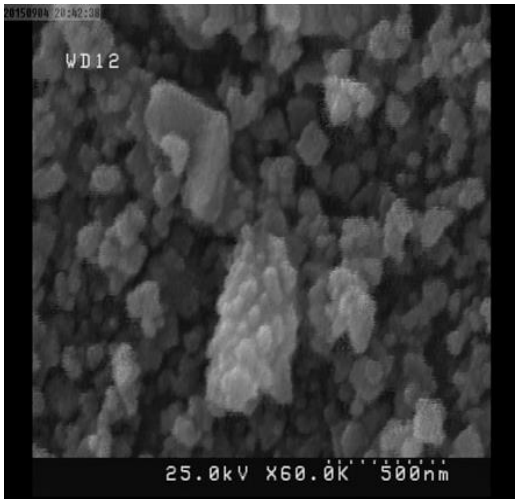
Figure 1: XRD diffraction of SnO2 thick film.

The morphology of the films was studied by FESEM, the pictures show homogeneous distribution with relatively high porosity due to deposition method. Also the grain size (Image J program) ranging between 40-70 (nm).

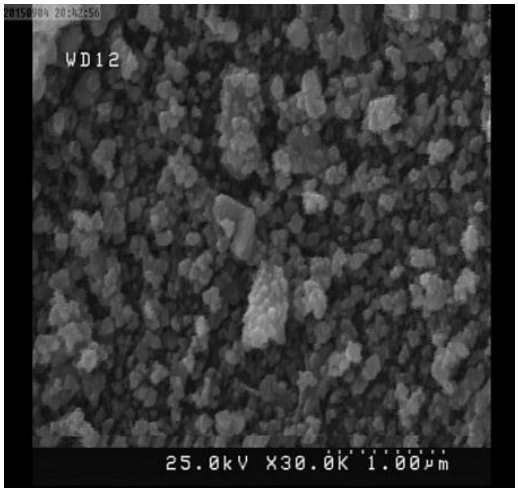


(a)

(b)



(c)



(d)

Figure 2: FESEM pictures for SnO2 film.

The optical properties of the screen printed thick film deposited on a glass substrate were studied with UV–Visible light using shimatzu–visible spectrophotometer. The films show high transmittance in range between (350 -600) (nm) as shown in Figure 3.

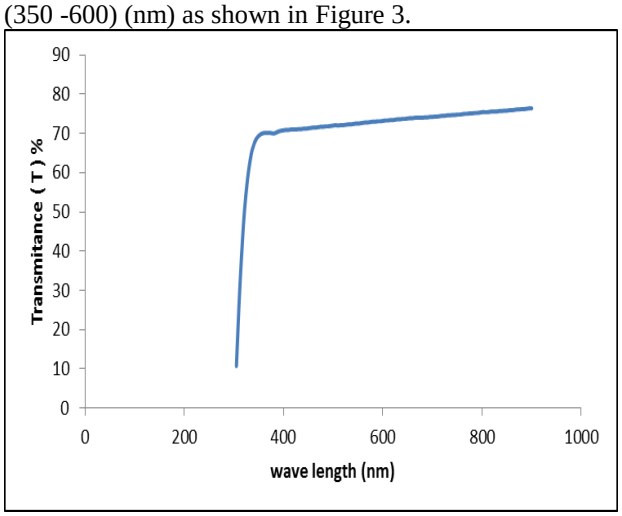


Figure 3: Transmission VS wave length.

The optical transition of SnO_2 crystals is known to be a direct transition so the absorption coefficient α is obeys the relation [16]:

$$\alpha(h\nu) \propto (h\nu - Eg)^{1/2}/h\nu$$

Plots of $(\alpha(h\nu))^2$ versus hν can be obtained from the data as shown in figure 4 The intercept of the tangent to the plot gives approximated value of the energy gap of the direct band gap materials it was found 3.83eV.

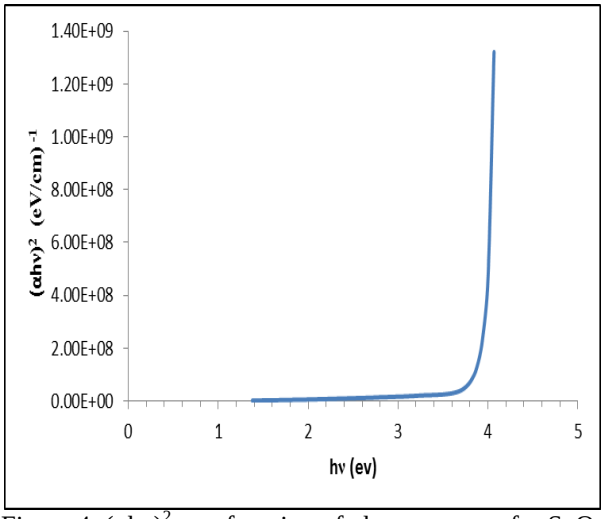


Figure 4: $(\alpha h\upsilon)^2$ as a function of photon energy for SnO_2 thick films.

Figure 5 shows the variation of photoluminescence emission intensity of SnO_2 with energy of illumination wave length, a strong green emission band was observed around 518 nm with an energy gap of 2.39 eV This emission is refer to the crystal defects or the electron transition occurs by defect levels such as oxygen vacancies, tin interstitials and so on in the band gap during the growth, oxygen vacancies are known to be the major defects and usually act as radiative positions in luminescence processes The oxygen vacancies existing in three different charge states V_o^0, V_o^+ and V_o^{++} in the semiconductor oxides [17, 18]. As V_o^0 is a very thin donor, the most oxygen vacancies will be in their paramagnetic V_o^+ state under thick-band conditions. Hence, the origin of the green emission band in the PL spectrum of SnO_2 nanostructure is because of the recombination process of electrons in the singly occupied oxygen vacancies with photo excited holes in the valance band vacancies. In the present SnO_2 nanostructure, the defects, such as oxygen vacancies, it act as luminescent positions, forming defect levels lying highly in the gap, attract electrons from the valence band enhance the luminescence [19].

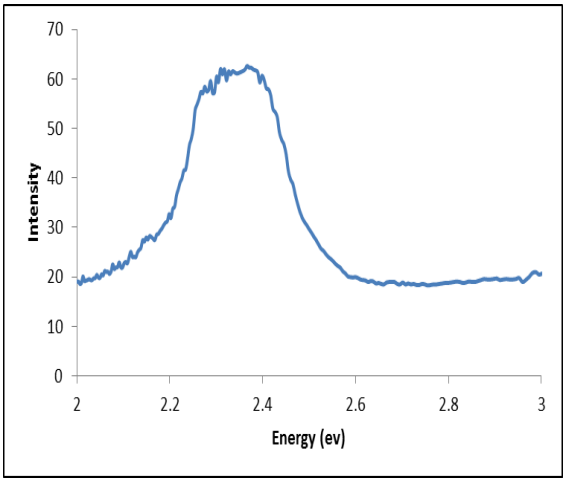


Figure 5: Room Temperature PL of SnO_2 Thick Film.

After film characterization the sensor was synthesized by electroding it with silver (IDE) electrode using screen prints method. The sensor exposure for different concentrations of Methanol Figure 6 and Acetone Figure 7 inside the chamber, the sensor shows higher sensitivity for Acetone and relatively faster response and recovery comparing with Methanol [20]. Also the operating temperature was investigated for both Acetone and Methanol; the obtained results were illustrated in Table 2.

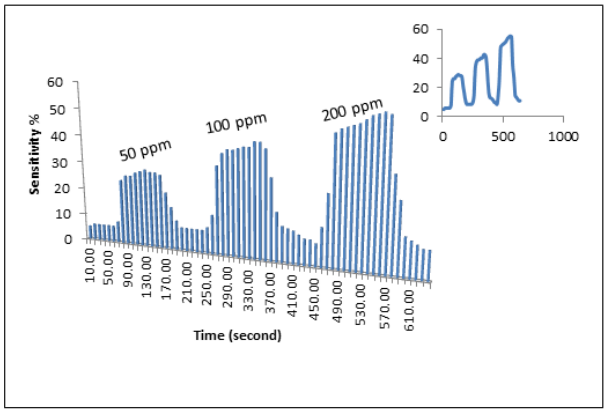


Figure 6: Change of Sensitivity of SnO_2 thick film with time for different concentrations of methanol.

Table 2: Response, recovery, and operating temperature of Acetone and Methanol.

Gas	Response time(sec)	Recovery time(sec)	Operating temperature
Methanol	**80**	**110**	**200 ^{0}C**
Acetone	**60**	**90**	**175^0 C**

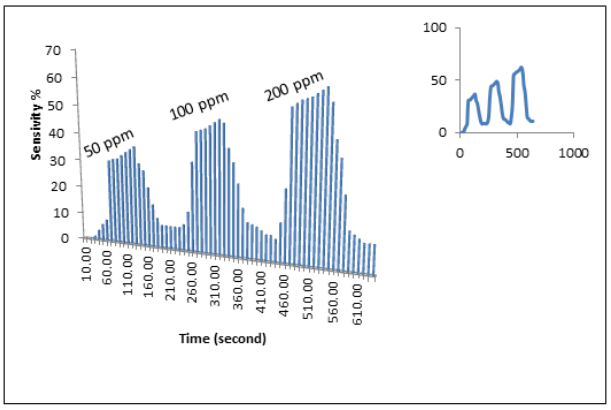


Figure 7: Change of Sensitivity of SnO_2 Thick Film with time for different concentrations of Acetone.

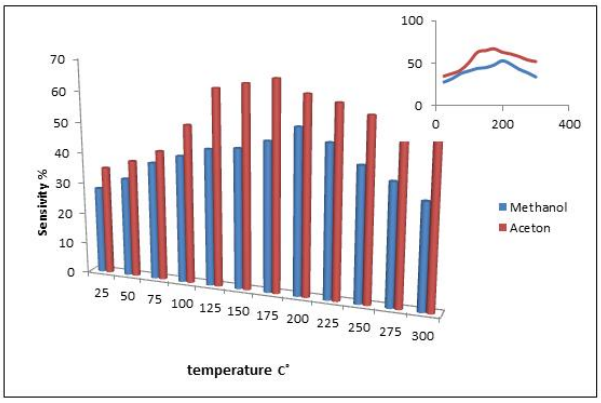


Figure 8: Change of Sensitivity of SnO_2 Thick Film with temperature at 100 ppm of Acetone and Methanol.

CONCLUSIONS

In summary, SnO_2 nanostructures were synthesized from Sn powder by simple evaporation method with Ar gas flow at atmospheric pressure The temperature in the furnace was rapidly raised up to 800 ^{0}C kept for 60 min The optical direct band gap estimated its found around 3.8eV The microstructures of the SnO_2 nanowires were characterized The morphology of the products depends on the preparation conditions (flow rate, temperature and heating time). The room temperature PL spectra of the SnO_2 nanostructure with high porosity screen print film showed a strong green band emission at 518nm with a band gap of 2.39eV, which is connected with oxygen vacancies or surface defect states, sensing parameters for Acetone and Methanol were estimated the results indicate it is promising for use in sensing devices.

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