

EFFECTS OF SURFACE MODIFICATION ON THE RECOVERY TIME AND STABILITY OF NANOSTRUCTURED TIN OXIDE THICK FILMS GAS SENSORS

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Abstract Along with high sensitivity in detecting gas, the response and recovery times of semiconductor gas sensors are of considerable importance for real life applications. In most cases, the recovery time is more than the response time. At the same time, water vapor present in the ambient, is chemisorbed on the tin oxide, SnO₂ surface and the water molecules dissociate into hydroxyl species, which act as electron donors. In this research, we find that if the interference of absorbed moisture can be reduced by surface treatment with thiourea diluted solution, the recovery time and stability of tin oxide sensors improves, which makes them suitable in real life applications.

Keywords Thick Film Gas Sensors; Thiourea; Tin Oxide; Sonochemical

چکیده علاوه بر حساسیت بالا نسبت به گازهای آلاینده، زمانهای بازیابی و پاسخ حسگرهای گازی نیمه هادی (نظیر اکسید قلع) از اهمیت قابل ملاحظه ای برخوردار هستند. در اکثر موارد، زمان بازیابی بیش از زمان پاسخ است. ضمناً بخار آب موجود در محیط می تواند روی سطح اکسید قلع (SnO₂) جذب شیمیایی شده و لذا مولکول های آب به ذرات هیدروکسیل تجزیه می شوند. این ذرات می توانند به عنوان دهنده الکترون عمل نمایند. در این تحقیق، دریافت شد که اگر برخورد رطوبت جذب شده توسط عملیات سطحی با محلول رقیق تیواوره کاهش داده شود، زمان بازیابی و پایداری حسگرهای گازی بر پایه اکسید قلع بهبود یافته و آنها را برای کاربردهای طولانی مدت مناسب می سازد.

1. INTRODUCTION

With increasing world- wide distribution of gas sensors for different applications, the demand of sensors fulfilling specific standards is growing in leaps and bounds. Because of their high sensitivity and ease of fabrication and handling [1-5], the tin oxide based semiconductor gas sensors are widely used to detect very low concentrations of combustible and pollutant gases like carbon monoxide, methane, hydrogen sulphide, hydrogen and ethanol. Thick film tin oxide gas sensors appeared in the market more than thirty years ago [3,4]. The main disadvantages of semiconductor sensors are their slow recovery and long term drift. It had been postulated that the long term drift in the resistance of a sensor is caused by the change concentration of adsorbed surface hydroxyl groups, due to variation in ambient humidity [6]. For tin

oxide sensors, at a temperature more than 160°C, slow dehydroxylation of tin oxide surface takes place as given below [7,8]:



It should be noted that above 160°C, instead of O₂⁻, O⁻ is the relatively stable species absorbed on tin oxide surface [7].

In addition, catalytic synthesis of H₂O₂ can also generate free electrons as given below [8]:



Both the reactions (1) and (2) are responsible for lowering the surface resistance of tin oxide sensors in humid atmosphere. The kinetics of such

dehydroxylation process at the operating temperature, normally 350°C, may not be fast enough as the extensive dehydroxylation happens only at about 400°C [9]. Hence, prolonged dehydroxylation at 350°C, can lead to a drift in electrical resistance of the sensors with time. To improve the long term stability of sensors only a few studies have been done, such as adding some dopants like TiO₂ into tin oxide powders [10] and surface modification with some modifier [11-13]. Morimitsu et al found that, the long term stability of the sensor (Tin oxide for CO detection) can be improved by surface modification with H₂SO₄ [11], H₂SO₄ plus catalysts like Pd, Pt, Ru and thiourea solution [12-14]. The formation of the sulfate species possibly block or reduce the active sites for the formation of the surface hydroxyl groups. It is interesting to see whether such conclusion is valid for tin oxide sensors containing Sb₂O₃ and Pd, where the former is added to lower the resistance of the sensors in real life applications, and the latter as a catalyst for detection of methane. Also, will be worthwhile to see whether surface treatment can improve the response and recovery time of the sensors.

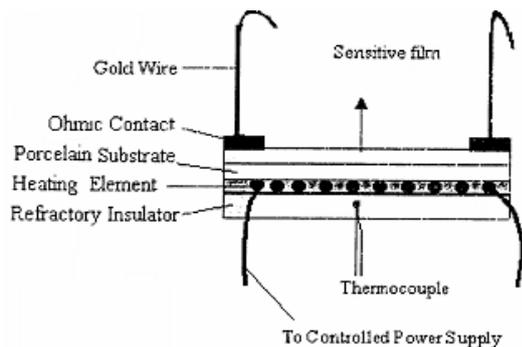
2. EXPERIMENTAL PROCEDURE

A batch containing tin oxide, 0.25 % (by weight with respect to tin oxide) antimony oxide and 10 % by wt, Pd was prepared by sonication assisted simultaneous precipitation technique. The composition of the powder [15] was selected, keeping in view the role of Pd as a catalyst to improve the sensitivity and the role of Sb as an n-type dopant to enhance the carrier concentration. In sonication assisted simultaneous precipitation technique, reagent grade SnCl₂·2H₂O, Sb₂O₃ and PdCl₂ were used as raw materials. Initially, Sn, Sb and Pd chloride solutions were prepared [10] and mixed in the calculated ratio and the mixture was taken in a beaker. The solution was sonicated (by ultrasonic processor, Vibronics, 25Khz, 250 W) for 30 min at a time after adding NH₄OH solution and the warm solution (pH = 9) was allowed to cool for 15 min. This sonication procedure was continued for 6 h. At the end of the reaction, a black precipitate was obtained. The precipitate was

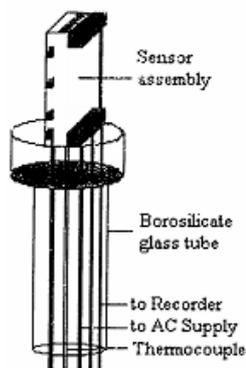
centrifuged, washed with distilled water and ethanol in sequence. The precipitate was again sonicated in ethanol for 10 min. and finally the ethanol was evaporated by slow heating to obtain a dry powder. The dried powder was annealed at 900°C for 2 h. in air.

A thick paste of the powder was prepared in an aqueous media containing a small amount (5 wt %) of PVA binder. The paste obtained was coated onto alumina plate as the substrate. The metallization was carried out by a paste printing of a high temperature conductive epoxy resin (Duralco-124). Two electrodes of 2×4 mm² were deposited on each device. Thin gold wires were cemented to the metallized area by the same epoxy. The sample was then gradually heated up to 200°C for epoxy curing and contact stabilization. The metal contacts were tested to be ohmic. The substrate was then attached to a temperature-controlled micro- heater, and was mounted on a refractory stand, so that the temperature of the substrate could be adjusted in the 25-450°C temperature range. The structure of the device is schematically presented in Figure 1a. A sensor probe was formed by mounting the sample on a thick-walled borosilicate glass tubing through which , two insulated connection cables were guided to the temperature control unit and the impedance measurement device respectively, Figure 1b. For each sensitivity measurement, the sensor probe was set at the desired operating temperature (see below) and a 10 min. time was allowed for the probe temperature to stabilize. Then, a constant AC voltage (10 v, 80 HZ) was applied to the sensor, while the current passing through the device was recorded. DC fields could cause ionic migration and electrode instability which were of much lesser concern in the case of AC voltages applied. The sensitivity measurement was then achieved by insertion of the probe into a three liters borosilicate glass tank containing air with a predetermined contamination level. To avoid errors caused by condensation of the contaminating gas on the walls of the tank, it was externally heated up to 50°C. The surface treatment of the material was performed by dipping the substrates into 0.1 mol/dm³ thiourea solution (for 1 min.) and then curing at 600°C for 5 min.

Simultaneous differential scanning calorimetry



(a)



(b)

Figure 1. Schematic illustrations of the fabricated gas sensor (a) and the sensor probe (b).

and thermogravimetric (DSC/TG) analyses (Netsche STA429) were carried out in the 20-700°C temperature range, with a heating rate of 5°C/min in dynamic air and FTIR measurements (Nicolet, SX800) were performed using a Brucker Tensor-27 spectrophotometer in the wave range of 400-4000 cm^{-1} .

X-ray diffraction (XRD) studies were performed on the powders in a 2θ scan configuration, of 20-80° 2θ range, at a fixed incident angle of 0.5°, using the $\text{CuK}\alpha$ radiation.

The electrical resistance and methane sensitivity of the coatings were measured at different temperatures (up to 450 C by placing a heating coil inside the coated alumina tubes) in an ambient humidity of 60-70 % by using a digital multimeter (Solarton), and a constant source of electrical current (Keithly 228A) and an X-Y recorder

(Yokogawa). All the samples were initially aged at 350°C for 3 days to achieve the desired stability before the measurements. Impedance studies were made by using EG and G 273A in the frequency range of 42 HZ-2 MHZ.

3. RESULTS AND DISCUSSION

Figure 2 shows the DSC/TG curves from the measurements, performed on pure SnO_2 powders. An endothermic region is observed at temperatures lower than 200°C in which two peaks appear. These endothermic phenomena, and the corresponding large mass loss, evidenced by the TG curve, can be attributed to the desorption of solvents and the elimination of chlorine from the powders. The curves for doped powders did not show a different structure with respect to the curves in Figure 2.

Figure 3 shows the XRD patterns of the sensor compositions before and after thiourea treatment. As expected, it is evident that there is no change in the XRD spectra of the two powders. The average crystallite size of the powder was 35 nm. The crystallite size was obtained from the XRD

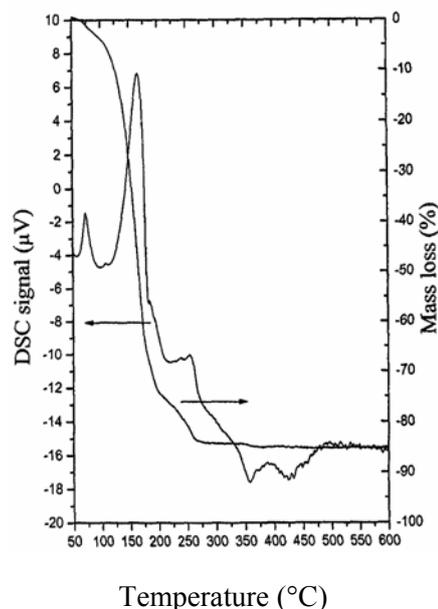


Figure 2. DSC/TG curves for a pure SnO_2 powder.

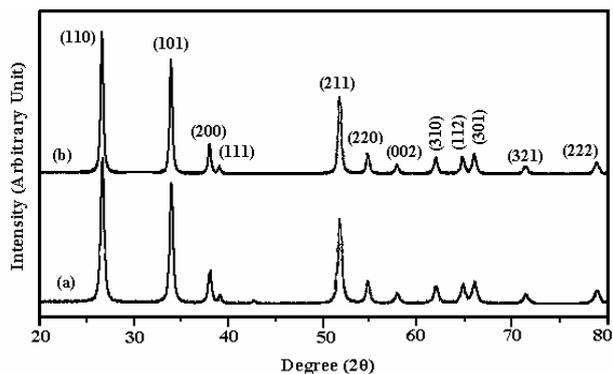


Figure 3. XRD patterns of the SnO₂ based powders (a) before and (b) after thiourea treatment.

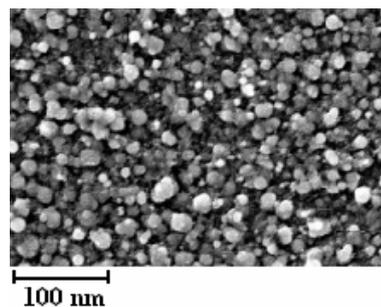
spectral peaks using Scherrer formula [16]:

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (3)$$

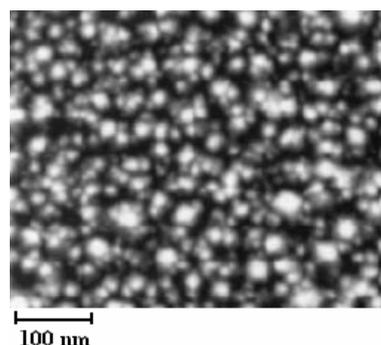
Where D is the average grain size, $\lambda = 1.54 \text{ \AA}$ (X-ray wavelength), and $\beta = (B^2 - b^2)^{1/2}$, B being the width of the diffraction peak at half maximum for the diffraction angle 2θ and b is the same for very large crystallites. The value of b was determined from the large grained XRD sample prepared by annealing the powder at a high temperature. Hence, it can be concluded that after thiourea treatment no marked change occurred in the structure and the crystallite size powders.

The surface morphology of the powders before and after thiourea treatment is given in Figure 4. The figures reveals that tin oxide powders before and after thiourea treatment, have exhibited modular and spherical crystals. No morphology change is observed when the surface modification with thiourea is used. As can be seen, the average size of the sphere shaped crystallites is 35 nm which corresponds to the result obtained from XRD patterns.

In order to understand the nature of the species on the SnO₂ surface, the IR spectra of the powders (sensor composition) were recorded. The absorption bands (Figure 5), located in the spectral region of 500-700 cm⁻¹ for both powders, are caused by the stretching modes of Sn-O or Sn = O in SnO₂ [17].



(a)

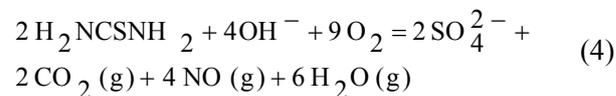


(b)

Figure 4. SEM images of tin oxide powders before (a) and after (b) thiourea treatment.

The bands of Sn-O (Sn = O) did not show any shift due to thiourea treatment. In Figure 5b, the absorption band in the region of 1030- 1200 cm⁻¹ is attributed to SO₄²⁻ group [18].

The following reaction has been envisaged on SnO₂ surface in presence of thiourea [19,20]:



The thiourea treatment is expected to reduce the density of OH⁻ group adsorbed on SnO₂ surface. At the same time, it can be seen from the inset of Figure 5 that the band attributed to hydroxide at 3400 cm⁻¹ decreases after treatment with thiourea solution.

The percentage response, S, in the methane has

been calculated as:

$$S = \left[\frac{(R_A - R_G)}{R_A} \right] \times 100 \quad (5)$$

R_A and R_G are the sensor resistance in air and methane (at 350°C), respectively. It has been found that after thiourea treatment no marked change had occurred in the percentage response of the sensor (around 85 % response at 1000 ppm methane).

The recovery time of the sensors are depicted in Table 1. It is interesting to note that thiourea treatment significantly improves the recovery time of the sensors. The response time of the sensors was around 10 sec. and therefore, was almost independent of thiourea treatment.

The formation of sulfate species probably enhances the recovery time because of the active sites for the formation of the surface hydroxyl groups are blocked or reduced, hence relatively labile O^- and O^{2-} species control the reaction time with ambient gases. At a high temperature (Table 1), the recovery time of the sensors is better because of faster kinetics and easier desorption of hydroxyl species.

The dependent properties of an insulator is generally described by complex impedance plots, where the impedance Z^* is given by:

$$Z^* = Z' - i Z'' \quad (6)$$

Where Z' and Z'' being the real and imaginary parts of the impedance, respectively.

Figure 6 shows the complex impedance spectra of the sensors in dry and wet atmosphere after thiourea treatment. In general, the effect of humidity on the resistance of the sensors depends on the amount of water vapor present in the air, the type of gas and the type of dopant introduced in the gas sensor [21]. From Figure 6, it is evident that the absorption of SO_4^{2-} species due to thiourea treatment, dramatically reduces the humidity effect of the sensors.

The equivalent circuit for the impedance plots in the present case is given in Figure 7, where R_{gb} and C_{gb} are the grain boundary resistances and capacitances, respectively. The optimum values of resistance (R_{gb}) and capacitance (C_{gb}) obtained for

the sensors under different conditions are given in Table 2.

Also, it is demonstrated in Figure 8 that the sensors treated with thiourea showed excellent long term stability with a very little drift in resistance. As discussed earlier, it is presumed that the long term stability of the sensors is attributed to the generation of the sulfate species on the sensor surface, which blocked or reduced the surface hydroxyl groups.

4. CONCLUSION

It can be concluded that after thiourea treatment no marked change occurred in the structure and the size of the crystallite powders. Also, no morphology change is observed when the surface modification with thiourea is used. It has been observed that thiourea treatment improves the recovery time and long-term stability of the sensors which make them suitable for real life applications. Also, the response time of tin oxide sensors treated by thiourea remains almost constant.

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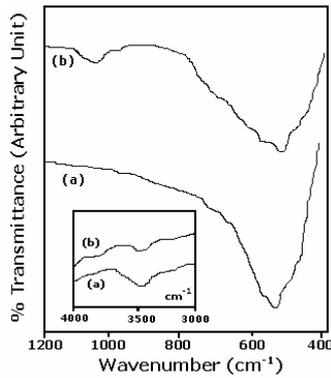


Figure 5. IR spectra of the sensor composition. (a) powder before thiourea treatment and (b) after thiourea treatment (inset-spectra in the range 3000-4000 cm^{-1}).

TABLE 1. Recovery Times of the Sensors in 1000 ppm Methane Under Different Operating Temperatures.

Working Temperature ($^{\circ}\text{C}$)	Recovery Time (sec)	
	Before Thiourea Treatment	After Thiourea Treatment (0.1 mol/dm^3)
300	230	115
350	190	95
400	150	90
450	100	85

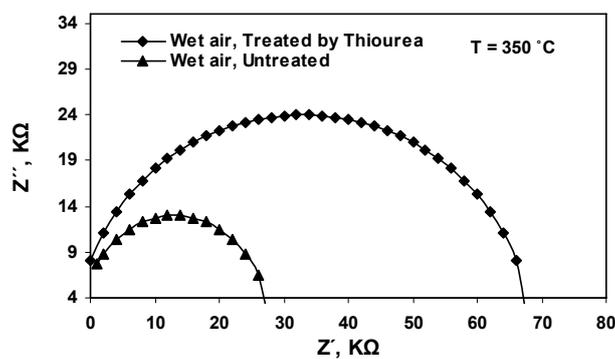


Figure 6. Effect of thiourea treatment on the complex impedance spectra of SnO_2 -based sensors in wet ($\text{RH} \sim 100$) air.

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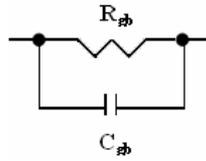


Figure 7. Equivalent circuit used for analysis of the impedance plots.

TABLE 2. Values of Resistance (R_{gb}) and Capacitance (C_{gb}) of Sensors under Different Conditions.

Condition	R_{gb} (k Ω)	C_{gb} (pF)
Dry Air	76.14	1.96
Wet Air (Treated)	68.01	1.64
Wet Air (Untreated)	28.15	1.77

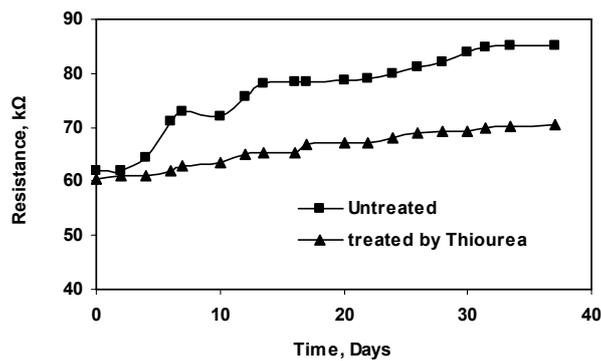


Figure 8. Stability of the sensors after thiourea treatment.

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