

THICKNESS DEPENDENCE OF SENSITIVITY IN THIN FILM TIN OXIDE GAS SENSORS DEPOSITED BY VAPOR PYROLYSIS

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Abstract Transparent SnO₂ thin films were deposited on porcelain substrates using a chemical vapor deposition technique based on the hydrolysis of SnCl₄ at elevated temperatures. A reduced pressure self-contained evaporation chamber was designed for the process where the pyrolysis of SnCl₄ at the presence of water vapor was carried out. Resistive gas sensors were fabricated by providing ohmic contacts on the layers obtained and the installation of a custom made micro-heater beneath the substrate. The sensitivity ($S = R_a/R_g$) of the fabricated sensors to acetone vapor contamination was measured at 270 °C. S increased linearly with contamination level up to 8000 PPM, and saturation was observed at higher concentrations. The experimental relationship between S and thickness of the sensitive film was investigated in films obtained by CVD for the first time. It was shown that S was inversely related to the film thickness, and higher S values were recorded for thinner sensors. The upper limit for S was imposed by the conduction instabilities observed in the thinnest films deposited.

Key Words Gas Sensor, Resistive Gas Sensor, Sensitivity, Tin Oxide, LPCVD

چکیده لایه نازک اکسید قلع بر روی زیر پایه پورسلانی (porcelain) به روش LPCVD نشانده شد. مبنای عمل، هیدرولیز بخار SnCl₄ بر روی زیر پایه داغ بود که در یک محفظه تبخیر کم فشار اجرا گردید. نشان داده شد که حداکثر حساسیت (R_a/R_g) در دمای ۲۷۰°C حادث می شود. بررسی تغییرات حساسیت برحسب مقدار بخار استن در هوا نشان داد که این ارتباط تا حدود ۸۰۰۰ PPM نزدیک به خطی است. ارتباط بین حساسیت و ضخامت لایه حساس نشانده شده به روش CVD عملاً مورد مطالعه قرار گرفت. نشان داده شد که حساسیت با کاهش ضخامت لایه حساس افزایش می یابد. ارتباط کمی بین حساسیت و ضخامت نمای است و امکان حصول حساسیت های بالاتری را در لایه های باز هم نازکتر پیش بینی می نماید. عملاً مشخص شد که حد بالای حساسیت به دلیل عدم پایداری هدایت الکتریکی، در نازکترین لایه های نشانده شده حادث می گردد.

1. INTRODUCTION

Transparent tin oxide thin films have been used for many different electronic applications [1]. Their use as resistive gas sensors [2-4] has recently been further spread due to a cost reduction, enhancement of the quality factors [5-6] and advances in the deposition techniques applied [7]. The sensitivity (S , see Section 3 for definition) of these gas sensors, however, is usually lower than

those of porous bulk [8-9] or thick film [10] resistive gas sensors. This is owing to the fact that in these devices the interaction between the target gas and the sensor takes place at the apparent surface of the sensitive film only. It is generally believed that by fabrication of thinner sensitive layers gas sensors of higher sensitivities can be fabricated. This concept has been experimentally verified in the case of gas sensors fabricated by spray pyrolysis technique [11]. However, no

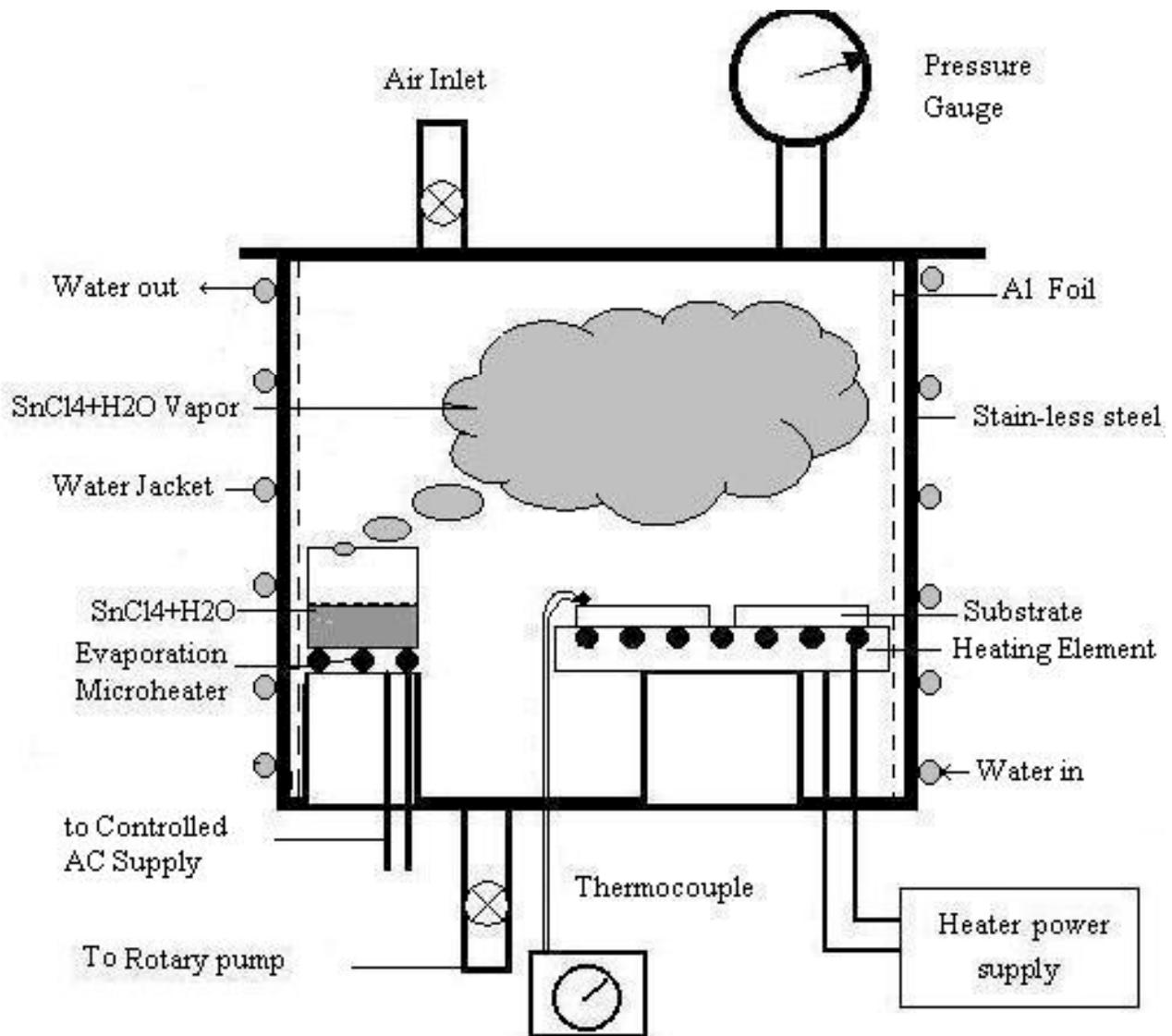


Figure 1. The schematics of the LPCVD system employed.

experimental data regarding the thickness dependence of the sensitivity in the case of the gas sensors fabricated by more elaborate deposition techniques is yet available.

The hydrolysis of tin tetrachloride precursor [12] has been used for gas sensor fabrication by other workers [11-13]. They have employed the spray pyrolysis of a water solution of the precursor [11-13]. The process has been carried out either in air [11-14] or in an inert atmosphere [15], both at atmospheric pressure. These processes are carried

out in open chambers, and control of the process to produce films of predetermined specifications requires intricate equipment and clean conditions.

In this work we have fabricated thin film tin oxide gas sensors by hydrolysis of SnCl_4 vapor on a hot substrate surface in a reduced pressure evaporation chamber. By benefiting from the positive features of a closed and self-contained chamber, tin oxide thin films of different thickness could reproducibly be deposited on porcelain substrates. This fabrication system has a smaller

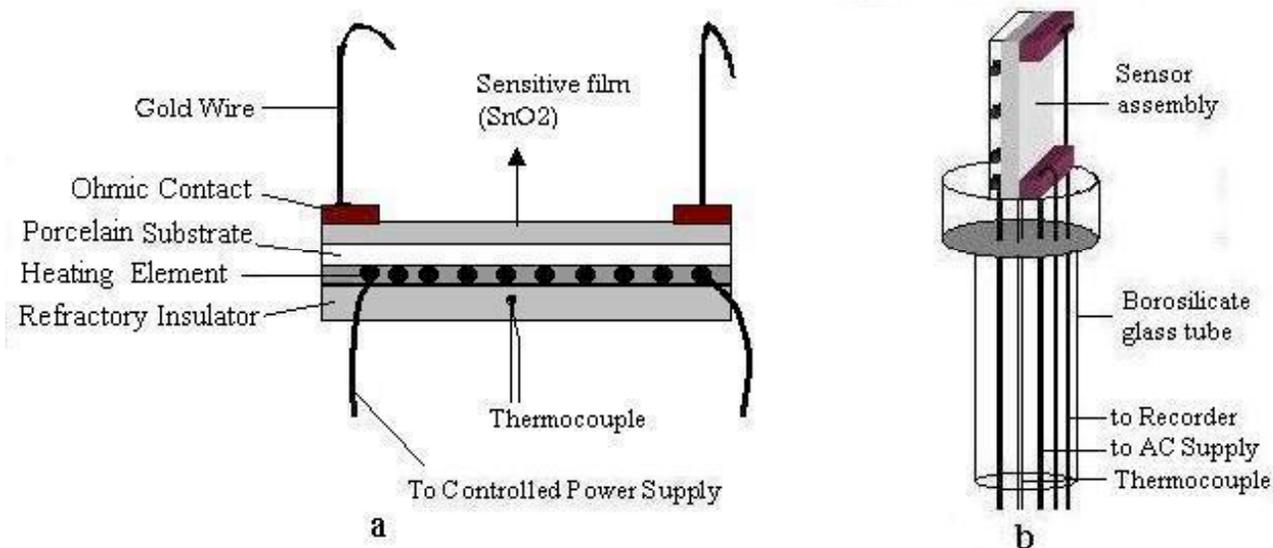


Figure 2. Schematic illustrations of the fabricated gas sensor (a), and the sensor probe (b).

number of the process parameters to be monitored or controlled, and a lower degree of cleanliness is demanded as the system is closed.

The sensitivity of the electrical resistance of the fabricated layers to acetone vapor contamination was measured for samples of different thickness. The results indicated a profound increase in the gas sensitivity due to a reduction in the thickness of the sensitive layer. A phenomenological quantitative relationship was derived to fit the experimental outcome. A comparison of the results by similar information regarding the other fabrication techniques has proved fruitful in understanding of the potentials as well as the limitations of the proposed fabrication technology.

The first aspect of the present work is regarding a custom designed low pressure chemical vapor deposition technique (LPCVD) for deposition of SnO₂ layers. The method is cost-effective, controllable, and affords reproducible fabrication of SnO₂ layers in a certain thickness range. The second aspect of the work, however, is related to gas sensor assessment, and more specifically addresses the thickness dependence of the sensitivity in the fabricated gas sensors. This part of the work provided the experimental relationship

between S and thickness of a CVD produced sensitive film for the first time, and clarified the potentials and limitations of the technique proposed.

2. EXPERIMENTAL

Materials “Extra pure” Cl₄Sn₅H₂O of 98% purity (Sigma-Aldrich, 14550) was used as the precursor. A supply of 5 w% solution of SnCl₄ in deionized water was prepared and kept in an airtight borosilicate glass container. This was the only source of precursor used in our experiments, so that the amount of the consumed precursor in different deposition runs could be estimated or compared based on the volume of the supply solution consumed. The substrates were made of high voltage grade siliceous porcelain (Maneh, Iran), cut and polished into 10x20x1.5 mm³ dice. In some specific experiments substrate of the same material with dimensions of 20x40x1.5 mm³ were employed. The deionized water used for the solution preparation and substrate surface cleaning was of 10¹⁰ ohm.cm resistivity. High temperature

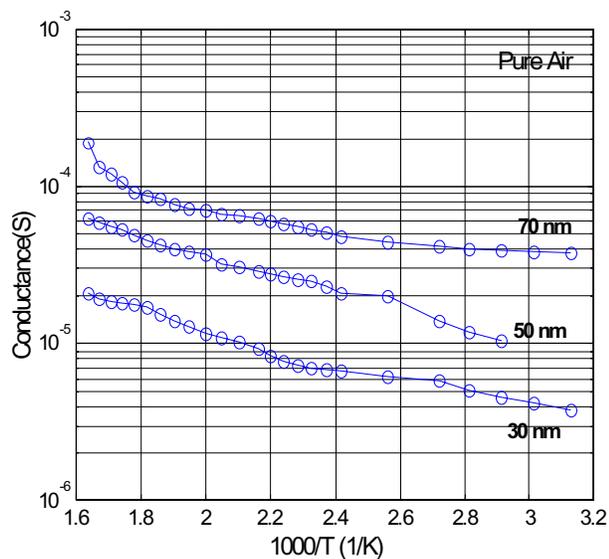


Figure 3. The temperature dependence of electrical conductance in three samples of different thickness.

epoxy conductive paste (Duralco-124) was used for printing ohmic contacts and gold wire connections. All of the heating elements inside the deposition chamber were made of Al-Cr-Fe alloy (Kanthal, A-1). The thermocouples used were K-type, and the heat insulating material employed to support the substrate heater was made of Al₂O₃-SiO₂ fiber board (Cotronics, 360HS). The acetone used as the target gas in our sensitivity measurement experiments were of “residue analysis” grade (MERK, #12).

Deposition Tin oxide thin films were deposited by a LPCVD [16] technique. One of us has previously reported graphite deposition by a similar method [17]. The system employed is schematically shown in Figure 1. The deposition is carried out in an airtight water-jacketed cylindrical stain-less steel chamber. The chamber pressure could be reduced down to 500 pa by a rotary pump. The substrates were kept at 350°C using a temperature controlled heating element. The actual substrate temperature was monitored by a thin thermocouple placed on the surface of a dummy substrate. A borosilicate capsule, containing a known volume, e.g. 5 cm³, of the supply solution was placed on a heater inside the deposition

chamber. The internal wall of the chamber was covered by aluminum foil which was replaced before each deposition. This prevented the re-evaporation of the condensed precursor and pyrolysis products to occur. Prior to each deposition run, time was allowed for the chamber evacuation down to 2000 pa and two successive argon purgings. The deposition started upon heating the precursor capsule to 60 °C. The test runs carried out by a gradual evaporation of the precursor solution at room temperature, resulted in inconsistent films and the process was hardly reproducible. The precursor evaporation increased the equilibrium pressure of the chamber which remained constant till depletion of the capsule from the solution. The observation of a reduction in the chamber pressure was a sign of completion of the deposition process. Then the heaters were switched off and air was allowed in through the air inlet. In these experiments all the parameters of the system including temperature of the capsule, substrate temperature and evacuation rate were kept constant. However, the above defined deposition time depended on the amount of precursor introduced into the chamber. Films of different thickness were deposited by altering the volume of our supply solution in the evaporation capsule. A detailed relationship between the thickness and morphology of the layers produced and the deposition conditions employed will be reported elsewhere.

Sensor Fabrication and Measurements The experimental relationship between thickness and sheet resistance in SnO₂ thin films deposited by SnCl₄ pyrolysis has extensively been studied by Korotcenkov et al. [11]. With respect to this relationship, an average thickness for a deposited film can be estimated by measurement of its sheet resistance. Resistive gas sensors are large area devices and a localized thickness measurement technique may introduce considerable error. However, the technique described resulted in an average (or effective) thickness over the active area of the sample which proved to be more reliable than the standard thickness measurement techniques. The sheet resistance of each sample was measured by a four point Van der Paw method [18], at room temperature and in pure air. The same measurement technique was employed at

elevated temperatures for the investigation of the temperature dependence of the conductivity in the deposited films.

The metallization was carried out by paste printing of a high temperature conductive epoxy resin (Duralco-124). Two electrodes of $2 \times 4 \text{ mm}^2$ were deposited on each device. Thin gold wires were cemented to the metallized area by the same epoxy. The samples were then gradually heated up to $200 \text{ }^\circ\text{C}$ 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 $150\text{--}450 \text{ }^\circ\text{C}$ temperature range. The structure of the device is schematically presented in Figure 2a. 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. For each sensitivity measurement, the sensor probe was set at the desired operating temperature ($270 \text{ }^\circ\text{C}$ in most of the experiments, see below) and a 10 min time was allowed for the probe temperature to stabilize. Then, a constant AC voltage (10v, 80Hz) 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 the insertion of the probe into a 3 lit 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 $50 \text{ }^\circ\text{C}$.

3. RESULTS AND DISCUSSION

Temperature dependence of the electrical conductivity was studied in three samples of different thickness. Results are presented in Figure 3 as $1/R$ vs. $1000/T$. The obtained curves being lines of equal slopes, is an indication of the prevalence of an identical major carrier generation mechanism and similarity of the compositions in

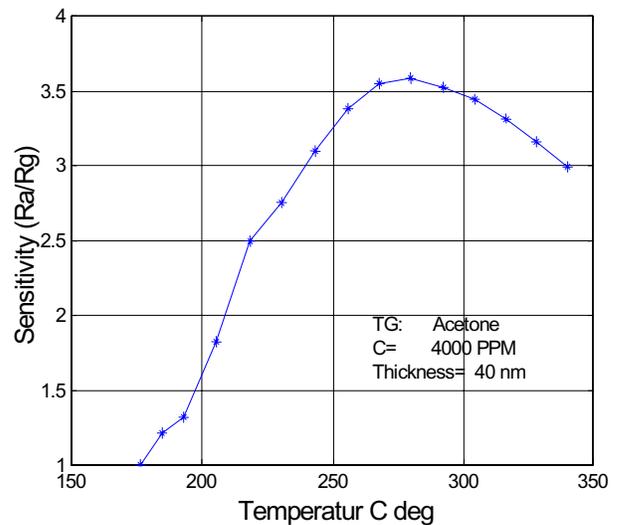


Figure 4. The experimental relationship between the sensitivity and operating temperature in the gas sensors fabricated.

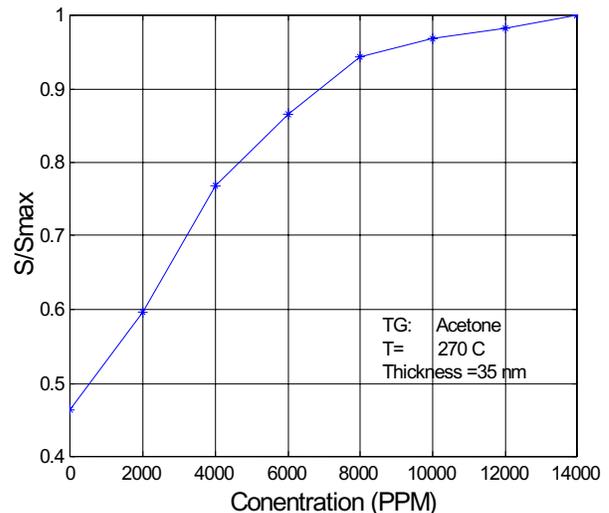


Figure 5. Variations of the sensitivity vs. acetone concentration in a sample gas sensor fabricated.

the films deposited [19]. The activation energy of the carrier generation could be estimated from the slope of the lines produced. It resulted in $46 \pm 4 \text{ meV}$, which is in agreement with the results reported for SnO_2 layers by other workers [20].

Different definitions of the sensitivity of a gas

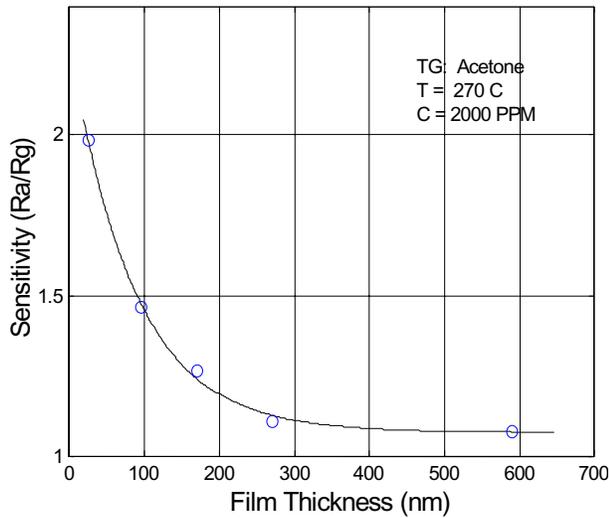


Figure 6. The experimental relationship observed between the sensitivity of the fabricated gas sensors and the effective thickness of the tin oxide layer employed.

sensor to a particular target gas have been presented in the background literature [2, 21, 22]. However most recently, the authors of the related technical papers have almost unanimously employed $S = R_a/R_g$ [2, 21], in which R_a and R_g are the steady state resistances of the sensor in pure and gas contaminated air, respectively. According to this definition, R_g and R_a should both be measured at the operating temperature of the device, respectively.

S is temperature dependent, and tin oxide based gas sensors are operated at elevated temperatures. S increases with temperature as the interaction at the gas-solid interface is accordingly enhanced. However, at a certain temperature the thermal carrier generation mechanism over shadows the same caused by the interaction with the target gas. Also the thermal desorption of the target gas molecules from the sensitive surface at higher temperatures becomes more significant and hinders the solid-gas interaction required for carrier generation [3]. Hence, it is important to find the maximum sensitivity temperature for the sample devices fabricated. In Figure 4 the results of our sensitivity measurements at various operating temperatures is presented. In these experiments the target gas was acetone at a concentration of 4000

PPM, and the device had effective sensitive layer thickness of 40 nm. It was concluded that the maximum sensitivity of the fabricated sensor occurred at the temperature range of 260 – 290 °C. This is in agreement with the results of similar measurements reported by others for thin film tin oxide sensors fabricated by different techniques [21]. Accordingly, the rest of our measurements were carried out at a constant sensor temperature of 270 °C.

The sensitivities of a sample device to various acetone concentrations were measured. The sensitive layer of the sample was 35 nm thick. The results are presented in Figure 5, indicating an almost linear increase in sensitivity with increasing target gas concentration up to 8000 PPM. A saturation of sensitivity is observed for higher contamination levels, as reported by others [7].

It was observed that the sensors fabricated with SnO₂ films of higher sheet resistances are more sensitive to the target gases examined. The concept of obtaining higher sensitivities from thinner sensitive films can be qualitatively explained based on the fact that the thinner films are of higher surface area per unit volume of the sensitive material. However, a quantitative analysis of this relationship requires ample source of experimental data. The sensitivity measurements involving one particular sensor sample, like those carried out for results presented in Figure 4 and Figure 5 are of routine experimental procedure. However those involving more than one sample are intricate and cumbersome owing to the instabilities encountered with each sample. That is to say, the gas sensing properties of thin film sensors are prone to changes caused by atmospheric poisoning, stress annealing, aging, metal ion diffusion from the electrodes, and thermal cycling induced problems at the film-substrate interface. These are the technical difficulties encountered with semiconductor thin film resistive gas sensors in general [3, 23] which make a comparative assessment of different samples difficult.

In order to keep the fabrication and test conditions as similar for the different samples as possible, a graded thickness film was deposited. The thickness varied over the length of a 40 mm long rectangular substrate. This was achieved by an angled stainless steel mask appropriately positioned over the substrate. Sheet resistances in

five lateral positions, delineated with a diamond pen, were measured and their respective average thicknesses were extrapolated as described in Section 2. The rest of the fabrication and sensitivity assessment for the five samples were carried out simultaneously, at 2000 PPM acetone contamination. The results of sensitivity measurements on these samples are plotted vs. the effective thickness in Figure 6.

The obtained data indicate a continuous increase of the sensitivity due to the thickness reduction. A natural extension of the graph obtained predicts even higher sensitivities for sensors of yet thinner sensitive layers. An attempt to deposit thinner layers was unsuccessful owing to the unstable films resulted. In other words, the upper limit for the sensitivity was practically imposed by the conduction instabilities observed in the thinnest samples deposited. Hence, further experimental work to obtain thinner but structurally and electrically stable layers is justified.

On the other hand, Figure 6 indicates that the gas sensors made of tin dioxide films thicker than 300 nm, are less prone to specification changes originated from structural instabilities. In this range, S is almost independent from the thickness of the film employed, and more reproducibility on device specifications can be achieved. However, it is clear that the films of this thickness range are unable to provide higher S values, and other procedures of S enhancement should be investigated [3,4].

The experimental relationship presented in Figure 6 is best covered with an exponentially decaying function. This empirically obtained curve is indicated as the solid line in Figure 6. We have analytically described the experimental relationship obtained; results are reported elsewhere [24].

4. CONCLUSION

Tin oxide thin films were deposited on porcelain substrates using a simple and cost-effective LPCVD technique. These films were employed for the fabrication of tin oxide resistive gas sensors. Test devices were fabricated and their gas sensing

characteristics with respect to acetone vapor at different concentrations were measured.

The relationship between thickness and sensitivity in these devices was investigated for the first time. It was experimentally concluded that films thicker than 300 nm result in more reliable but less sensitive gas sensors. It was also shown that the thinner layers of tin dioxide provide sensors of higher sensitivity. That is to say, in choosing the thickness of the sensitive layer a trade off between sensitivity from one side and stability, reliability, and reproducibility from the other is in action. In practice, the upper limit for the gas detection sensitivity of these sensors was imposed by the electrical conduction instabilities occurring in the thinnest films deposited. Further development work regarding the refinement of the reported deposition technique for deposition of thinner but electrically stable films is recommended.

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