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Characteristics of Tin Oxide Nanostructures Deposited on Porous Silicon Substrates

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Abstract

In this work, nanostructured Sn_2O_3 thin films with different Cu_2O content (2-10 at.%) were prepared by pulsed-laser deposition (PLD) method. The film samples with 2, 4, 6, 8 and 10 at.% of Cu_2O showed Sn_2O_3 peaks of wurtzite structure. We have studied the operation temperature of gas sensors fabricated from the prepared samples at different etching times (5-60 min) and different environment temperatures (50-350°C) and found that the maximum sensitivity was about 79% for porous silicon prepared after etching time of 10 min.

Keywords: Gas sensor; Copper oxide; Tin oxide; Porous silicon
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1. Introduction

The artificial olfaction system is a very promising tool to monitor the off-odors in the field. Usual odor measurement techniques use human olfaction or conventional analytical techniques [1,2]. The first category represents the real odor perception but is not applicable to measure continuously bad odors in the field. The second class of techniques provides the mixture composition, but not the global information representative of the odor perception. The e-nose has the potentiality to combine “the odor perception” and the “field monitoring”. The instrument, based on non-specific gas chemical sensor arrays combined with a chemo-metric processing tool provides a suitable technique for in site monitoring of off-odors. The research group in Arlon has more than a decade of experience in the field measurement of environmental odors. Published studies report attractive results [3,4]. This technique has probably the best potentialities to answer to the expectations of the various actors of the environmental problems in relation with the odors annoyance [5]. However, a number of limitations are associated with the properties of chemical sensors [6,7], the signal processing performances and the real operating conditions of the environmental field [8]. The field experience of the research group has shown that the metal oxide based gas sensors are the best chemical sensors for long term application, more than one year of continuous work. However, as a result of harsh environmental conditions, hardware limitations and olfactory pollution specificities, real-time odor monitoring with the electronic nose is always a real challenge. The instrument has to cope with several specific drawbacks. In particular, it has to automatically compensate the time drift [9] and the influence of ambient parameters such as temperature or humidity [10]. This paper is focused on the time drift and the long term stability of the metal oxide gas sensors. Sensor drift is a first serious impairment of gas sensors. The sensors alter over time and therefore have poor repeatability, since they produce different responses for the same odor. That is particularly troublesome for electronic noses. The sensor signals can drift during the learning phase [11]. Another frequent problem encountered in the field and particularly in highly polluted atmosphere is the sensor failure or an irreversible sensor poisoning. Clearly, life expectancy of sensors is reduced in real-life operation when compared with clean lab operations. Sensor replacement is generally required to address such issue, but, after replacement, odors should still be recognized without having to recalibrate the whole system [12]. But commercial sensors are rarely reproducible. In order to appraise the time evolution of the sensors and the effect on the results of an electronic nose, experiments were performed during several years on two identical sensor arrays. The signals of two "identical" sensors array, placed in the same measurement chamber, were observed during several

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years. After a state of the art of the sensors drift correction techniques [13-20], the most relevant methods for the field has been tested and the results compared in order to select the best one for our application.

Metal oxide semiconductors have attracted significant attention in gas sensing applications due to their simple implementation, low cost, and good reliability for real-time control systems with respect to other gas sensors [21-28]. The gas sensing properties of metal oxide semiconductors are influenced by many factors such as their operating temperatures, morphology and chemical composition of the films [29]. In such gas sensors, the change in the electrical conductivity is due to the interaction of the targeted gas molecules (chemisorption or physisorption) with the surface of the metal oxide grains. Consequently, metal oxide sensors show changes in the resistance under exposure to oxidizing or reducing gases. [24,30]. Since the majority of these sensitive layers are n-type, p-type semiconductors sensitive to gases are highly demanded for gas sensing applications such as sensor arrays for electronic nose [31].

These p-type semiconductor gas sensors have much different sensing pattern from their n-type counterparts [32]. In addition, it is also reported that p-type semiconductors are more appropriate for detecting oxidizing gases such as nitrogen dioxide [33]. At elevated temperatures, the presence of chemically adsorbed molecules such as nitrogen dioxide can cause electron depletion at the surface of the metal oxide grains; and consequently, the electrical resistivity of the thin films increases [22]. The competition between chemisorptions of nitrogen dioxide and atmospheric oxygen, at the same active surface sites of the metal oxide layer, plays an important role in determining the specific nitrogen dioxide/metal oxide interaction [34].

The diffusion of copper into Sn_2O_3 can cause the formation of complex centers (Cu_{Sn}, Cu_i). It is possible that copper atoms can replace either substitutional or interstitial Sn atoms in the Sn_2O_3 lattice creating structural deformations [35,36]. Copper oxide significantly affects the electrical, chemical, structural and optical properties of Sn_2O_3, and the study of the electronic state of Cu in Sn_2O_3 was the subject of interest for a long time [37-39].

2. Experiment

Tin oxide powder with different doping concentrations for Cu_2O at (2-10) at.% Cu_2O pressing it under 5 tons to form a target with 2.5 cm in diameter and 0.2 cm in thickness. It should be as dense and homogenous as possible to ensure good quality Cu_2O:Sn_2O_3 thin films deposited at different doping ratios (2, 4, 6, 8 and 10 at.%) by PLD technique, whose experiments are carried out inside a vacuum chamber that initially evacuated down to 10^{-3} torr. The focused Q-switched Nd:YAG laser beam is incident at angle of 45° on the target surface. The substrate is placed in front of the target with its surface parallel to that of the target. The film thickness was determined by a Spectroscopic Reflectometer SR300 and found to be 120 nm with a tolerance of ±7 nm.

Layers of porous silicon (PS) were prepared by electrochemical etching where the silicon wafer serves as the anode, as shown in Fig. (1), while the cathode is made of platinum. Both are immersed in $HF/H_2O_2/H_2O$ mixture of 1:1:1 mixing ratio as an electrolyte. A p-type silicon wafer was used as a starting substrate in the photochemical etching. The samples were cut from the wafer and rinsed with acetone and methanol to remove dirt, as well as to remove the native oxide layer on the samples. The electrochemical etching process was carried out at constant current 40 mA and different times (10, 25 and 60 min).

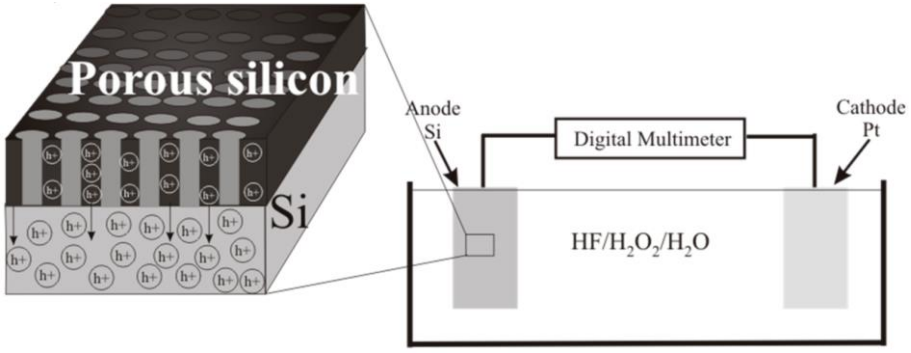

Fig. (1) Experimental setup to prepare porous silicon

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3. Results and Discussion

Figure (2) shows the sensitivity for nitrogen dioxide gas with 10 ppm concentration, as a function of operation temperature in the range of 27-350 °C for Cu_2O:Sn_2O_3 (0.98-0.02) wt.% which are deposited on porous (111) Si wafers at different etching times. It can be seen from Fig. (2) that the sensitivity of all films increases with increasing operating temperature to reach a maximum value corresponding to an optimum operating temperature of 150 °C for all samples. Beyond this temperature, the sensitivity to nitrogen dioxide gas of all samples decreases at about 350 °C. The high temperature operation of the sensor makes the lifetime of the sensor shorter and increase its resistance, thus more electrical power is required for operation. It is believed that the oxygen could be removed or lost from the bulk of the metal oxide materials at high temperatures. This suggests that the response of the sensor may decrease at higher temperatures since there will be more oxygen vacancies, which lead to less occurrence of the reaction between nitrogen dioxide and oxygen.

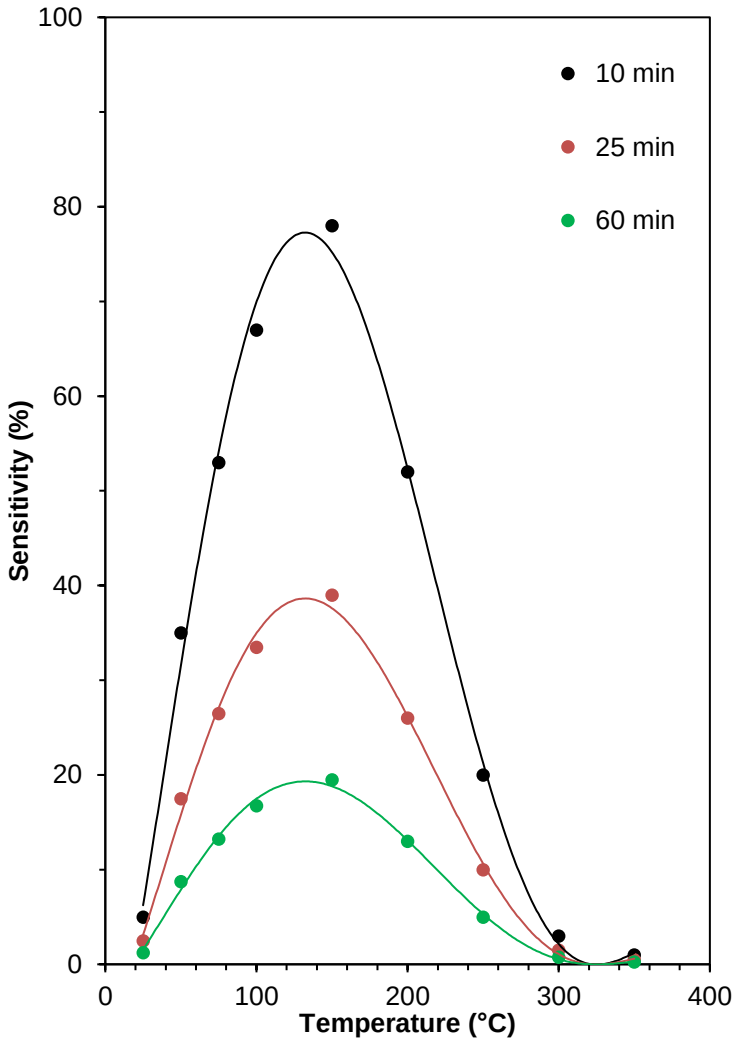

Fig. (2) Variation of sensitivity with operating temperature for different etching times on porous silicon

Decreasing etching time leads to increase the sensitivity of sensors to nitrogen dioxide gas and improve the sensor response at 200 °C. The sensing process depends on the surface roughness which increases detection sensitivity. The films prepared at porous times of 10 min have higher values of sensitivity because the surface roughness is high.

Figure (3) shows the variation of response time with porous time at different operation temperatures. This figure reveals that the response time decreases with increasing porous current at operation

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temperatures lower than 200 °C, while the response time increases with increasing porous time from 10 to 60 min at higher operation temperature (>200°C).

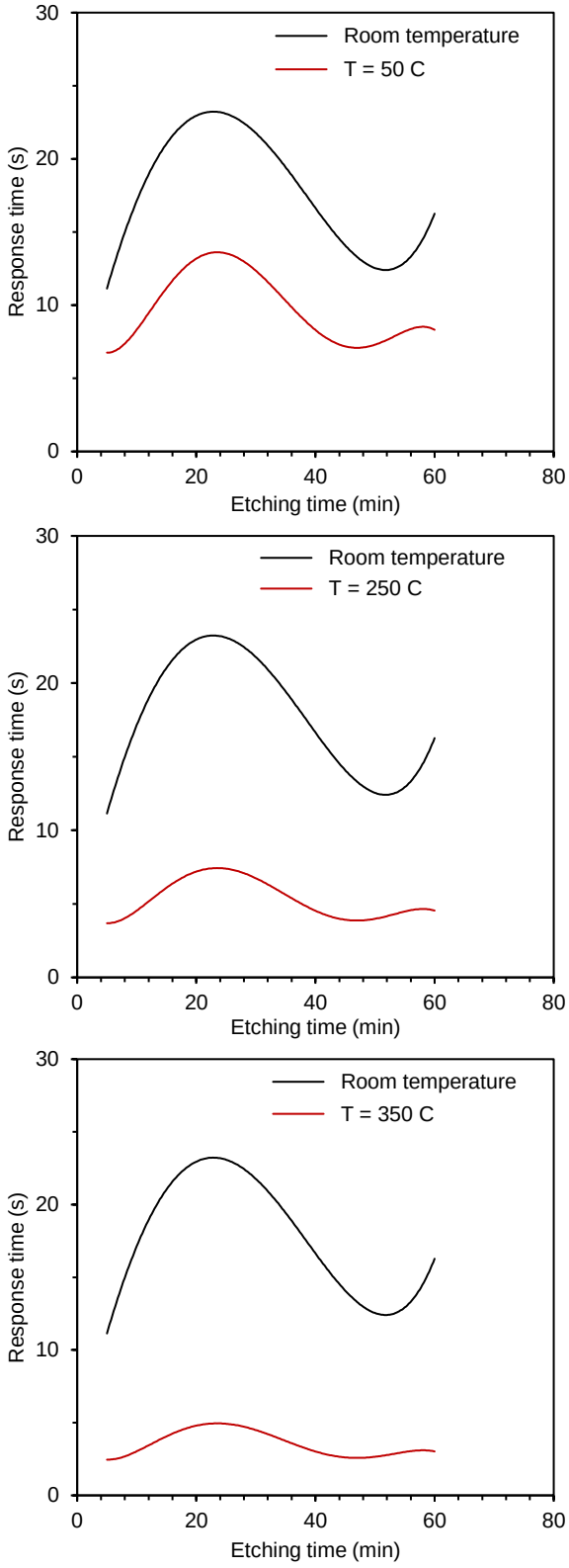

Fig. (3) Comparisons of response time variation with etching time at different operating temperatures with room temperature condition

The reduction in the grain size due to increasing porous time allows the space charge to cover large volume of the grain and the large number of grain boundaries provides large area for adsorption of O^-

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and O^{-2}. Hence, large variations in the barrier and resistance can enhance the reactivity at lower temperatures. Also, the density of surface states increases with the reduction in the particle size, or it can help in lowering the operation temperature.

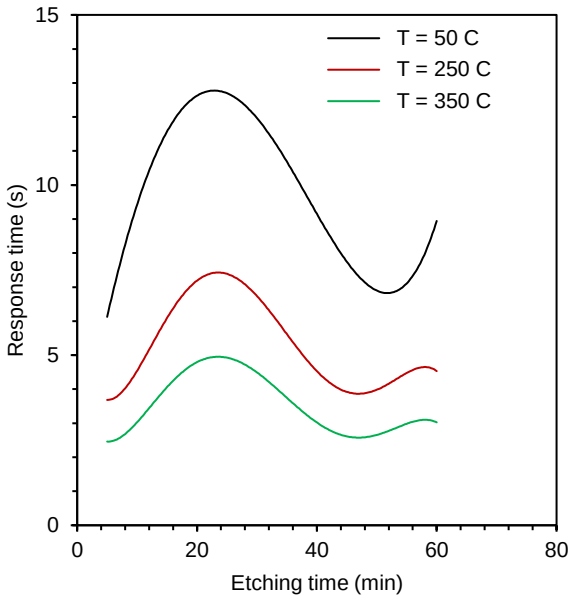

Fig. (4) Effect of operating temperature on variation of response time with etching time

4. Conclusions

In concluding remarks, polycrystalline Cu_2O-doped Sn_2O_3 structures were successfully prepared by PLD technique. We have studied the operation temperature of gas sensors fabricated from the prepared samples at different etching times (5-60 min) and different environment temperatures (50-350°C) and found that the maximum sensitivity was about 79% for porous silicon prepared after etching time of 10 min.

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