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Effect of Al_2O_3 on the morphological and gas sensing properties of SnO_2 pellets

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***Abstract*—** Alumina mixed tin oxide (SnO_2: Al_2O_3) powders were obtained by employing chemical and physical synthesis methods. The powders were prepared from tin chloride as Sn source, urea (R1) and ammonia (R2) as precipitant agents. The resultant SnO_2 powders are milled in a planetary ball mill. Finally, Al_2O_3 was added to the milled SnO_2 powders manually in different ratios, and then pressed to manufacture thin pellets. After several experimental trials, stable SnO_2: Al_2O_3 pellets were formed. Later, silver contacts were manufactured on the pellets surface by the thermal evaporation technique. The effect of Al_2O_3 ratio and precipitation agent on the morphological properties are presented in this work. The morphological study was developed by using Scanning Electron Microscopy (SEM). Additionally, the sensing properties of these pellets as a function of the SnO_2: Al_2O_3 ratio were measured in carbon monoxide (CO) atmosphere and a hypothesis model for an arrangement of SnO_2 and Al_2O_3 particles on the pellets surface for different mixing ratios is proposed.

Keywords*—Pellets; tin oxide; Alumina; Morphology; Sensitivity; CO.*

I. INTRODUCTION

The intention of preparing sensors is for improving the daily life and make it easier by inventing new skill full devices which will decrease the human effort to perform the same tasks quickly. In general, a sensor is a device that converts a physical phenomenon into an electrical signal. Intrinsically, sensors are the interface between the physical world and the world of electrical devices [1]. According to the International Electro-technical Committee (IEC), "The sensor is the primary part of a measuring chain which converts the input variable" [2]. To detect toxic gases, such as propane (C_3H_8) and carbon monoxide (CO), SnO_2 is one of the beneficial semiconductor materials. Main property of SnO_2 is its dual valency. Controlling the oxygen surface defects makes its resistance to change with respect to temperature and test gas concentration, which can be used for gas sensor signal [3].

A pellet sensor surface is more porous which increases the oxygen trapping and subsequently the surface conductance with respect to the operation temperature and the gas concentration [4]. The change in the conductance with and without gas serves as a sensor signal. Gas sensing mechanism is explained in detail by various authors [5-9].

SnO_2 is one of the most studied and convenient material for gas sensing applications because it has substantial chemical durability; it does not form stable chemical compounds with the particles absorbed; it possesses sufficient thermal and mechanical strength [10-12]. Significantly, SnO_2 is a broad band gap semiconductor which exhibit a high surface oxygen adsorption (if contrasted to elementary ones) [13], therefore, exceptionally high sensitivity is achieved because of their numerous electro-physical properties.

Generally, sensitivity of powders can be increased by doping. Numerous works have been done proving the doping is effective in increasing sensitivity, however it is difficult to identify the sensing process due to doping [14-17]. Also, in case of pellets the amount of material used is immense compared to films. Considering the above two factors, we have chosen alumina to mix with SnO_2 because as a ceramic material alumna does not affect the sensing process, increases the porosity of the pellet and preserves the SnO_2 material.

Controlled, simple and cost effective synthesis of nano-sized SnO_2 particles is achieved by utilizing homogeneous precipitation and ball milling methods [18]. Uniform particles with narrow size distribution is achieved by employing these methods [19].

In this study, that is a succeeding of four previously reported works [20-23], we manufactured SnO_2: Al_2O_3 pellets for sensing CO. The main objective of this work is to study the effect of the addition of Al_2O_3 to SnO_2 pellets, by different ratios, on the sensing properties. This is the first step in order to observe the effect of alumina really in sensitivity. In future, further optimization parameters are studied.

II. METHODOLOGY

II.a. Preparation of SnO_2 powders

In our previous works [20, 21], synthesis, ball milling and pellet manufacturing conditions of SnO_2 powders by using precipitant agents, urea (R1) and ammonia (R2) were explained in detail. In this work we have utilized the optimal conditions

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that were reported in the referred works [20, 21] for mixing alumina.

After ball milling of SnO_2 powders, milling time and speed were optimized to 6h and 400rpm, respectively. Later, the milled powders in both routes (R1 and R2) were mixed with alumina, Al_2O_3, (Sigma Aldrich) manually in a mortar with SnO_2: Al_2O_3 ratios such as 1:0, 1:1, 2:1, and 4:1. The idea for mixing the alumina is both to save the SnO_2 powders and for increasing the oxygen trapping. Pellets were manufactured from processed SnO_2: Al_2O_3 powders. Powders were pressed by using a manual pressing machine. The optimal pressing conditions for getting stable pellets, after several trials, were 16 tons during 90 min.

II.c. Characterization

Scanning electron microscope (SEM), by using an AURIGA equipment, was employed to examine the morphological characteristics and the particle size of the calcined agglomerates. Additionally, SEM was also employed to analyse the surface morphological characteristics of all synthesized powders.

The sensing properties of the pellets were determined by electrical conductance measurements developed in a home-made system. The conductance changes were registered by using a Keithley 2001 multimeter. The experimental setup for measuring the electrical resistance is previously reported in our work [23].

The measurements were made at three different operating temperatures, namely, 100, 200, and 300°C. Lower operation temperatures do not lead to conductance changes. For measuring the electrical response in CO, pure silver ohmic contacts, by using a pellet holder and a steel mask, were deposited on the pellets surface by the thermal evaporation technique. The sensitivity of the pellets, *S*, was obtained by calculating the electrical resistance ratio by using the following equation (1).

$$S = R_{gas}/ R_{vac} \text{ -------- (1)}$$

Where R_{vac} is the measured resistance in vacuum ($5*10^{-1}$ mbar), and R_{gas} is the resistance measured in presence of CO at different concentrations varying from 0 to 300ppm ($5*10^{-1}$m to $2.7*10^{2}$bar).

III. Results and Discussion

III.a. Sensing properties

The effect of change in alumina ratio on the CO gas sensitivities were plotted in the Fig. 1. Alumina mixed SnO_2 pellets does not show significant changes in the sensitivities when measured at 100 and 200 ^{0}C. At lower temperatures since the adsorbed oxygen species were less reactive, the sensitivity obtained is very low.

In Fig. 1, the sensitivities plotted were obtained at temperature 300 ^{0}C and for 300 ppm of CO concentration. From this figure, we can observe that, the sensitivities decrease after mixing alumina compared to pure SnO_2 pellets and this is because of the decrease in the amount of SnO_2. The maximum sensitivities achieved were around 48 and 34 for pellets prepared by R1 and R2, respectively, and when mixed with ratio 2:1. Sensitivity depends not only on porosity but also on the amount of sensing material.

By considering both porosity and quantity of sensing material, we explain the sensitivity changes after mixing with alumina. Calculated % SnO_2 (sensing material) and porosity theoretically in each alumina mixing case and reported in Table. 1. Porosity (P) [24] is calculated by using equations 2-4.

Where m and v are mass and volume of the samples, n is number of molecules per unit cell, M is molecular weight and NA is Avogadro's number. Similar results were obtained for powders prepared by R2. Thus form the above observations, theoretical calculations and the sensitivity graphs, a hypothesis arrangement model of SnO_2 and Al_2O_3 atoms on the surface is depicted and shown in Fig. 2.

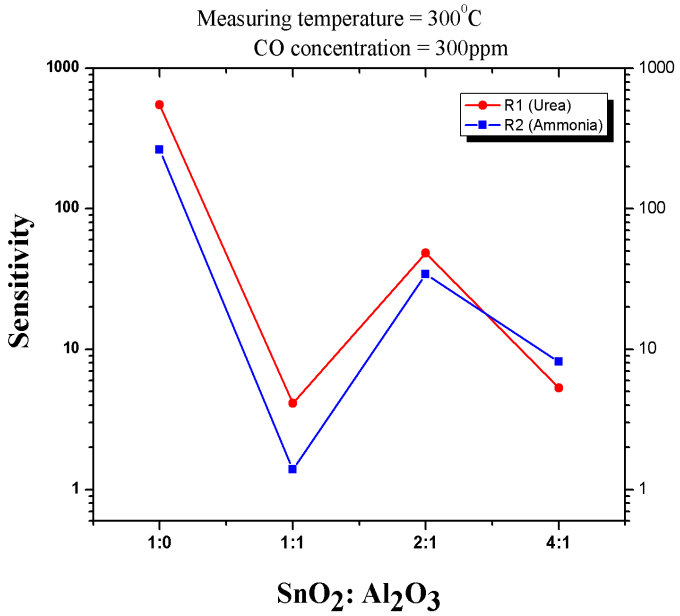

Fig. 1. Comparison of sensitivities of SnO_2: Al_2O_3 pellets for different mixing ratios.

$$P = (1 - \frac{\rho_a}{\rho_x}) \times 100\% \quad (2)$$

$$\rho_a = \frac{m}{v} \quad (3)$$

$$\rho_x = \frac{nM}{N_A V} \quad (4)$$

SnO_2:Al_2O_3	Quantity of SnO_2 (%)	Porosity (%)
1:0	100	32.30277
1:1	33.33	54.35864
2:1	66.66	74.62565
4:1	83.33	60.01781

Table. 1. Porosity and quantity of sensing material in all alumina mixing ratios for powders prepared by R1.

Therefore, from Fig.1, Fig.2 and Table.1, the following details can be observed:

a) In case of 1:1, sensing material is very less and porosity is less compared to case of 2:1 which may reduce the sensitivity.
b) In case of 4:1, porosity is less compared to case of 2:1, thus the oxygen trapping is lesser in 4:1 than 2:1, which would decrease the sensitivity.
c) 2:1 is the best case compared to 1:1 and 4:1, where the sensitivity is very high because, availability of enough sensing material and also high porosity compared to all remaining all case, including pure. Oxygen trapping increases due to high porosity.

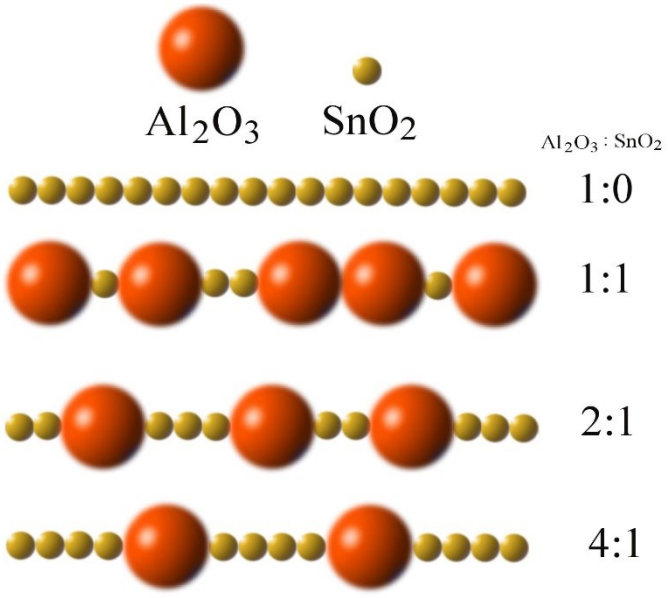

Fig. 2. A hypothesis model for an arrangement of SnO_2 and Al_2O_3 particles on the pellets surface for different mixing ratios.

III.c. SEM analysis

In order to cross check our hypothesis model, we have performed the SEM analysis of the 2:1 mixed pellets surface. Fig. 3 shows the alumina mixed tin oxide pellets surface prepared by R1 at different magnifications. From Fig.3a, it can be observed that the SnO_2 particles with particles size around 20nm were homogeneously distributed all over the surface. In Fig. 3b, it is observed both the alumina and tin oxide grains, in which, the alumina particles were surrounded by the SnO_2 particles. The size of alumina particles is around 5µm, which is much larger than a SnO_2 particle. From Figs. 3c and 3d, it is clearly evident that the alumina and tin oxide particles were agglomerated separately. We assume that, this would have resulted due to the pressure applied to prepare the pellets made all the bigger grains to come closer and together.

Alumina, as a ceramic material, does not participate in sensing mechanism, the amount of sensing material in all the alumina mixed tin oxide pellets were decreased, which in turn reduces the sensitivity of the alumina mixed tin oxide pellets sensitivity compared to the pure tin oxide pellets. Hence the adverse effect of the Al_2O_3 mixed SnO_2 pellet sensitivities was a consequence of pellet preparation method. Further optimization of pressure and pressing time, is necessary to improve the performance of the alumina on the sensor response. Moreover, the composition of alumina and tin oxide inside the pellets should be analyzed and studied.

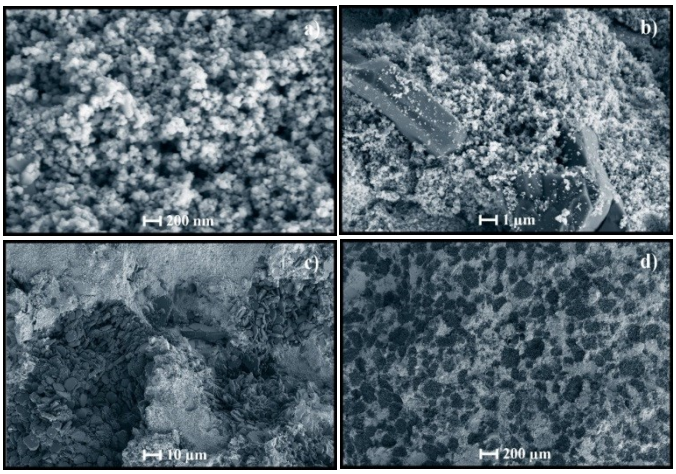

Fig. 3. SEM images of SnO_2 and Al_2O_3 mixed pellets surface at magnification of (a) 200nm, (b) 1µm, (c) 10 µm, and (d) 200µm.

IV. CONCLUSIONS

SnO_2 pellets were successfully mixed with alumina. SEM analysis reveals that, SnO_2 and Al_2O_3 have particle sizes around 20 nm and 5 µm, respectively. We believe that, the use of bulk doping cause very broad particle size with different faces of the particles. Additionally, an agglomeration of particles is observed. This may be due to the heating produced during the ball milling process.

CO sensitivity of the SnO_2: Al_2O_3 pellets observed only at 300 ^{0}C and were around 48 and 34 for pellets prepared by R1 and R2, respectively, and when mixed with ratio 2:1. In case of R1, the sensitivity is only registered follows electronic sensitization. For powders prepared by R2, the sensitivity is observed follows chemical sensitization. It is evident that

mixing alumina reduces sensitivity but the quantity of sensing material is saved. 2:1 mixing ratio of tin oxide and alumina is more beneficial due to presence of adequate porosity and sensing material.

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