

Development of ZnO-doped SnO₂ sensor for Detection of SO₂ and Performance Validation through Artificial Neural Network

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Abstract— In the present work we have fabricated a thick film SnO₂ sensor on a 1"x1" alumina substrate. It consists of a gas sensitive layer (SnO₂) doped with ZnO, a pair of electrodes underneath the gas sensing layer serving as a contact pad for sensor and a heater element on the backside of the substrate was printed. The sensitivity of sensor has been studied and measured at different temperatures (150^oC - 350^oC) upon exposure to SO₂. An approach is made to measure the sensitivity of ZnO-doped SnO₂ by using Artificial Neural Network tool. Finally we have shown the results that shows the potential of Artificial Neural Network as a design tool in the area of thick film gas sensor fabrication and development.

Keywords—Artificial Neural Network, Thick film sensor, sensitivity, ZnO

I. INTRODUCTION

Metal oxide semiconductor sensors based on electric conductivity measurement have been used extensively for gas detection. SnO₂ is most widely used material among semi conducting oxides for making gas sensors due to its low cost, long life and good reproducibility [1,2]. Tin oxides can be fabricated mainly into three types of devices i.e. sintered block, thick film and thin film[3]. Among these, thick film SnO₂ devices are most studied and most suitable candidate due to their high level of sensitivity, simple design, low weight and cost effectiveness. SnO₂ is an n-type, wide-band gap (3.6 eV) semiconductor [4]. Its electrical conductivity is due to the non stoichiometric compositions as a result of oxygen deficiency [5]. The sensing properties of the thick film gas sensor are based on the adsorption of the gas molecules on its surface which produce changes in their conductivity [6]. Thick film of SnO₂ consists of large number of grains of slightly different sizes, interconnected by Schottky barriers of different heights [7]. The Schottky barrier height is dependent on the surface charge density, which gets modulated due to adsorption of gas molecules [8, 9].

ANNs are collections of small individually interconnected processing units. Information is passed between these units along interconnections. An incoming connection has two values associated with it, an input value and a weight. The output of the unit is a function of the summed value. Once an ANN is trained for a prescribed data it may be ready to be used then for the prediction or classification. ANNs can automatically learn to recognize patterns in the data from real systems or from physical models, or other sources. An ANN can also handle many inputs and produce answers that are in a form suitable for designers [10].

In the present work for the recognition of the sensitivity of the ZnO-doped SnO₂ sensor Feed Forward Back Propagation Network has been used.

II. RELATED WORK

The sensor behavior based on reaction kinetics was created by Gajdo et al.[11]. The SnO₂ sensor is operated in the dynamic regime. The properties of the designed model were verified by experiments. The experiments were carried out with organic liquid vapours in air (ethanol, acetone, benzene, and hexane) and three different types of gas sensors TGS 813, TGS 82 and SO 91K.

Wang et al. [12] synthesized tin dioxide nano-crystals by a precipitation process and then used as the support for 2 weight % gold/ tin dioxide preparation via a deposition-precipitation method, followed by calcination at 200^oC. Thick films were fabricated from gold/tin dioxide powders, and the sensing behavior for carbon monoxide gas was investigated. The gold/tin dioxide was found to be efficient carbon monoxide gas-sensing materials under low operating temperature (83–210^oC). The Au/SnO₂ sensor with SnO₂ calcined at 300^oC exhibited better CO gas-sensing behavior than the SnO₂ calcined at other temperatures. The experimental results indicated the potential use of Au doped SnO₂ for CO gas sensing.

Metal oxide gas sensors were used for environmental monitoring of urban and industrial areas, where the pollution level may become dangerously high studied by Giberti et al.[13]. In this frame, environmental temperature plays a fundamental role, since it may influence the sensor signal. This work aims at measuring ambient temperature induced conductance variation, and to suggest a theoretical model to account for that.

The effect of Fe-doping on the surface chemistry and gas-sensing properties of nano-crystalline tin oxide was analyzed by Vaishampayan et al. [14]. The pristine and Fe doped SnO_2 were synthesized by the modified Pechini citrate route that produces around 40 and 18 nm sized nanoparticles, respectively. 1 at % Fe-doped SnO_2 shows significantly high selectivity towards hydrogen sulfide gas with capability to detect even 10 ppm of hydrogen sulfide at room temperature, with change of about one order of magnitude in the resistance within 5–15 s. In comparison, pristine SnO_2 shows negligible response towards H_2S at room temperature. The ideal response and recovery of Fe-doped SnO_2 at low concentration of gas suggests Fe-doped SnO_2 nanomaterial as a potential low cost, low temperature H_2S gas sensor.

III. METHODOLOGY

A. Preparation of Lead glass Powder

Lead glass powder is widely accepted glass matrix for thick film ceramic pastes. The main advantage of lead glass matrix is that its firing temperature is below 1000°C which is desirable for thick film fabrication technique. The main components of lead glasses are Lead monoxide (PbO), Silica (SiO_2), Alumina (Al_2O_3) and Boric Oxide (B_2O_3). Different types of lead glass are prepared using different combinations of these materials with lead mono oxide as major part. In preparation of lead glass, firstly, all the four components viz. lead oxide; silica, alumina and boric acid (all in powder form) are weighed according to their percentage and mixed for several hours in the ball mill. After mixing in ball mill, the mixture is poured into platinum crucible and is kept in a preheated furnace at 1200°C . In this process the mixture starts melting after about 2 hours to form a liquid phase and is allowed to remain at the same temperature for one hour for proper mixing in the liquid phase. After this the crucible is removed from the furnace and the charge of the crucible is quenched in cold water which results solidification of charge into lead glass.

B. Preparation of Tin Oxide Powder

The tin oxide powder used for gas sensors should be in nonstoichiometric form. In the process of preparation of tin oxide powder two widely accepted [15,16,17] methods are adopted, one is by the reaction of ammonia water with tin chloride and second is by reaction of nitric acid with tin metal. In the first method, the solution of tin chloride is prepared by dissolving granules of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ in distilled water. Now ammonia water (NH_4OH) is slowly added to the prepared solution of tin chloride with continuous stirring. After some time white precipitate of tin hydroxide [$\text{Sn}(\text{OH})_4$] appears. Further, the precipitate is filtered and dried in an oven at about 150°C . The powder thus obtained is tin hydroxide which is calcined at 400°C for four hours to get tin oxide. The schematic of fabricated gas sensor is shown in fig.1. Tin oxide was available in the form of indium doped tin oxide paste, supplied by Electro Science Laboratories (ESL3050, USA). This indium doped tin oxide paste (SnO_2) has been taken as the base sensing

material. The doped pastes were prepared by adding 1% ZnO (by weight) in base SnO_2 paste with cellulose based thinner. The thermistor pattern is screen printed first (paste NTC 2413 ESL), dried at a temperature of 1000°C and fired at 9500°C . In the second step, finger electrode pattern is screen printed using silver conductor paste (No. PD 6176, DuPont) and dried at a temperature of 100°C .

Subsequently, a heater element is screen printed on the back side of the substrate using silver palladium conductor paste (No. C1214, Heraeus, Gmbh) which is dried at the same temperature. Now the dried screen-printed films are fired at 8500°C . In the third step, ZnO-doped tin oxide paste was screen printed over the electrode pattern and the print was allowed to dry at a temperature 1000°C for 20min. The dried film was then fired in a thick film furnace (DEK model 840) in a set temperature profile with peak temperature zone of 5500°C .

The fabricated sensor was then exposed to varying concentration of acetone in a locally developed test chamber of volume 2047 cm^3 having placed at the metal base. The change in resistance of sensor is measured using KEITHELY 195A multimeter.

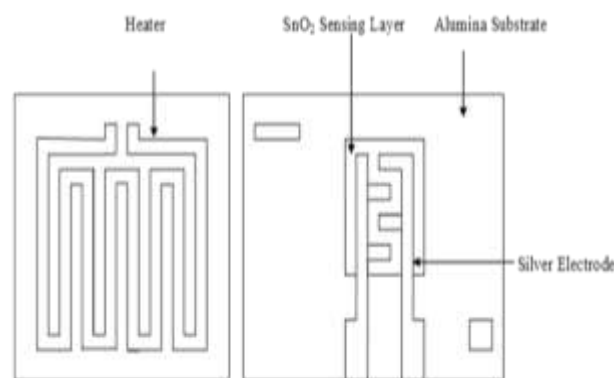


Fig.1 Schematic of fabricated sensors

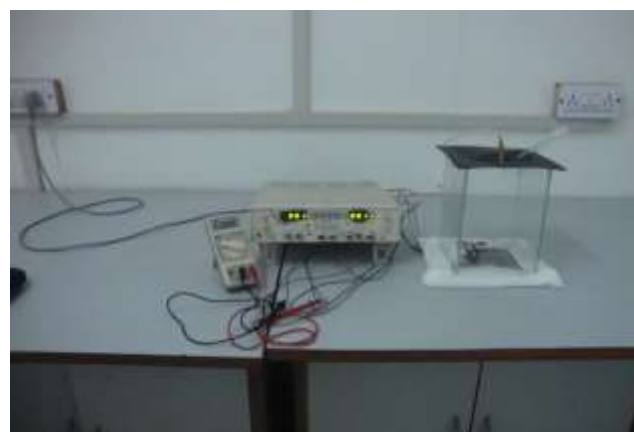


Fig.2 Developed Measurement Set up

IV. RESULTS AND DISCUSSION

The experimentally obtained data are first divided in two groups which is given in Table 1 and 2. The first one is

training data group by which we have to train the network and the next one is testing data group by which we have to test the network. Ten experimentally obtained data is used for the training and remaining three data sets at the concentrations at 1200 ppm, 1800 ppm and 2400 ppm were used for the testing. The test data set is not used during training. We have scaled the training target data (sensitivity) by the highest magnitude of the sensitivity and used these scaled values as training and testing of the network. The spread constant is changed during the experiment. Our goal is achieved at spread constant 0.1 and at 47 epochs. The output of the NN matches well with the experimental output.

Table.1 Training Data Set

Concentration (ppm)	Sensitivity of the Sensor	Scaled sensitivity of the Sensor
500	10.14	0.04
1000	45.75	0.43
1500	62.27	0.85
2000	72.25	0.91
2500	81.52	0.93
3000	90.75	0.94
3500	92.25	0.95
4000	93.15	0.97
4500	93.45	0.96
5000	93.89	1.0

Table.2 Test Data Set

Concentration (ppm)	Sensitivity of the Sensor	Scaled sensitivity of the sensor
1200	24.32	0.64
1800	33.82	0.89
2400	35.15	0.925

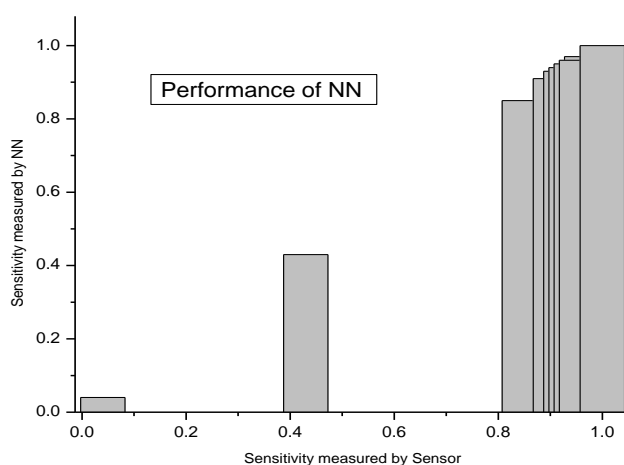


Fig.3 Performance of the Neural Network

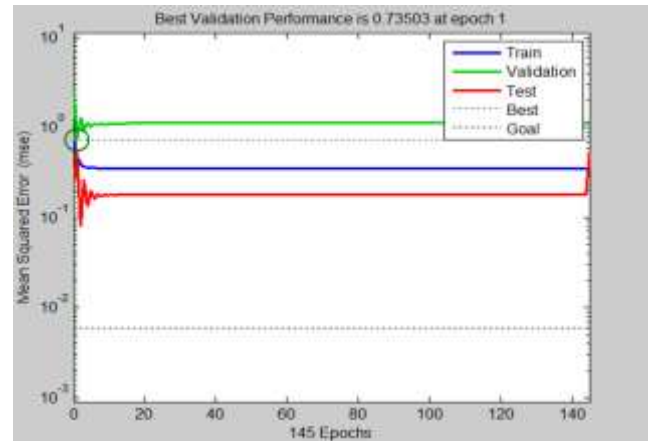


Fig.4 Results of validation performance in Purelin network transfer function

V. CONCLUSION

A thick film of tin oxide consists of grains connection to each other through grain boundaries. The migration of charge carriers through these boundaries governs the formation of schottky barriers at the interface between the grains. Through the bulk of the grains also affects the conduction process in tin oxide thick film, but mainly conduction is governed by schottky barriers at the grain boundaries. In air ambient, oxygen molecules are adsorbed on the sensor surface. When the sensor is exposed to a gas or odor to be detected SO₂ gas molecules get adsorbed on the sensor surface. The mutual reaction between the reactants (adsorbed oxygen and the gas molecules) leads to transfer to charge carriers. This modulates the barrier height leading to a corresponding leads to a corresponding change in the sensor conductivity.

In this paper we have Paper presents the recognition capability of the neural network. It describes the result for the best trained which has been used to model the realization between the experimentally obtained sensitivity of the ZnO-doped SnO₂ gas sensor and output obtained sensitivity of the NN model. NN trained for the different spread constants. Best result is obtained at spread constant 0.1. Thus, ANN may be used as design tool for the thick film sensors.

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