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Development of Pd-doped SnO_2 Thick Film paste for Gas Sensor

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Abstract

In the present work effort has been made to develop the thick film paste for gas sensor. In the first step glass powder has been prepared and then SnO_2 powder was synthesized. In the next step Pd-doping has been done and finally thick film SnO_2 sensor was fabricated on a 1″x1″ alumina substrate. It consists of a gas sensitive layer (SnO_2) doped with Pd , a pair of electrodes in array form underneath the gas sensing layers serving as a contact pad for sensor and a common heater element on the backside of the substrate. Alumina substrate (96%) has been used as a substrate for sensor fabrication. The fabricated sensor was tested for varying concentration of ethanol in a locally developed test chamber. The response of the sensor for varying concentration of ethanol tested the sensitivity of the sensor for ethanol.

1. Introduction

An increased concern over safety in civilian ones and industrial settings has generated great interest in semiconductor gas sensor for reliable gas detection in the past several decades. As environmental regulations become more stringent, the need to develop highly sensitive gas sensors grows. To meet the demand of low level gas detection, gas sensors should be upgraded in sensitivity, selectivity, stability and speed of response [1]. At the same time they should be cost effective and reliable over long term [2]. Thick film technology has the flexibility of varying the properties of the fabricated device by altering the shape and size of the component allowed by the screen printing process and the choice of the substrate [3]. The ability to attach discrete active and passive devices either in encased or chip form further enhances the versatility of thick film technology. Complete functional circuits from simple amplifiers to complete arrays containing many chip type monolithic ICs are possible in thick film form. Thick film technology also offers many advantages at high frequencies and has been utilized in circuits operated in Giga-Hertz range [3].

A thick film circuit is normally consists of layers of special inks (or pastes) deposited on an insulating substrate. The deposition technique for thick film circuit is essentially identical to that used for traditional silk screen printing and employs a screen consisting of finely woven mesh of stainless steel (nylon or polyester) to define the pattern for the various films. The mesh is coated with the ultra violet (UV) sensitive emulsion onto which the circuit pattern can be developed photographically. The ink is placed on the opposite side of the screen and a squeegee traverses the screen under pressure, thereby bringing it into contact with the substrate and also forcing the ink through the open areas of the mesh to the substrate. The next stage is to keep the wet print on a perfectly horizontal surface to promote print leveling follow by drying of the print to remove the organic solvents from the paste. This is usually done at a lower temperature range 100-125^{0}C. The paste is then fired in thick film firing furnace in accordance to the firing profile of the paste. The film themselves contains fine powders of tin oxide and glass frit, which must be exposed to high temperatures if they are to form a solid composite material and adhese permanently to the substrate. This is because during the firing cycle, the glass melts and forms a mechanical key at the film- to- substrate interface. It also provides the suitable matrix for the active material of the film. [4].

Thick film compositions are dispersion of inorganic oxide or metal powders in organic fluid vehicle systems. These compositions have three parts: functional or active phase, binder and vehicle. The functional or active phase can be a metal or semiconducting oxide powders for resistor compositions, metal powder for conductor compositions. The binder adhere the fired film to the substrate in a glass matrix. The organic vehicle is made up of volatile solvents and polymers or resins. The resin serves as a temporary binder to hold the unfired film together and makes it adhere to the substrate, and the solvents reduce viscosity and make the compositions screen printable. The composition of the organic vehicle determines (or helps to determine) the shelf life of paste, its drying rate on the screen, the change in printability with ambient temperature, some electrical properties of the fired film and their cosmetic appearance [4].

2. Experimental

2.1 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 [5]

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. To achieve the required powder of boric oxide, amount of boric acid was doubled as per following reaction:

$$2H_2BO_3 \longrightarrow B_2O_3 + 3H_2O + 1/2O_2 \uparrow$$

Boric Acid Boric Oxide

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.

Now lead glass pieces are crushed and grinded in a ball mill having 250 ml zirconia jar and 20 mm diameter zirconia balls to get glass powder. Further, the powder is sieved through a mesh having 300 holes per inch to get fine powder.

In the next step, the firing temperature of the lead glass is optimized as it decides the firing temperature of the final paste. To optimize the firing temperature, thick films of lead glass are printed on several alumina substrates and each substrate is fired at different temperature. By observing the adhesion of the fired film, the firing temperature of the glass is optimized.

2.2 Preparation of Tin Oxide Powder

The tin oxide powder used for gas sensors should be in non-stoichiometric form. In the process of preparation of tin oxide powder two widely accepted [6, 7, 8] 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 $SnCl_4.5H_2O$ 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 [$Sn(OH)_4$] appears in the form of reaction product is given below:

$$SnCl_4 + 4NH_4OH \rightarrow Sn(OH)_4 + 4NH_4Cl$$

In this reaction, excess ammonia is added to convert all tin chloride into tin hydroxide. After this the precipitate is washed thoroughly with distilled water so as to remove excess ammonia and ammonium chloride. 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 chemical reaction for the same is given below:

$$Sn(OH)_4 \rightarrow SnO_2 + 2H_2O$$

Tin oxide obtained by this method is yellowish in color.

2.3 Additives

The suitable conductivity of tin oxide is achieved by doping of antimony oxide (Sb_2O_3). This material increase the film as it fits active grains together to form a compact adhesive film on the substrate, but they have no catalytic property. Firstly, antimony oxide is weighed (10%) and mixed with tin oxide powder and is ball milled for two hours to get uniform mixing. To improve the gas selectivity, sensitivity and to lower the operating temperature of gas sensors, a small amount of noble metals such as Ag, Ti, Pd and Pt are doped with tin oxide as activators or sensitizers. Some metal oxides such as CuO, Bi_2O_3 , PbO, ZnO are also good catalyst dopant to enhance the sensitivity of the tin oxide sensor. To dope Palladium, palladium chloride ($PdCl_2$) is taken as starting material. Firstly, palladium Chloride ($PdCl_2$) is taken as starting material. It is then weighed (2%) and mixed with already prepared mixture of tin oxide and antimony oxide solution in a ball mill. After mixing the mixture, it is calcined at 800˚C for one hour. The calcination of the powder before the paste preparation and the firing process of the printed film determine the sensitivity of the active layer. With calcinations, grain boundaries are developed and powder sinters to bigger agglomerates causing the layer surface area after firing and by this way higher sensitivity of the layer.

3. Result and Discussion

3.1 Thick Film Paste

To get a proper paste for fabrication of thick film sensor, it is necessary to optimize the proper composition of glass binder, tin oxide powder, organic powder and the organic solvent. It is desirable to have minimum amount of glass powder in the paste because the role of glass matrix is only to provide adhesion between active material and the substrate. In similar manner, the amount of organic binder and its solvent are also optimized to get the required thixotropic properties of the paste for printing.

After optimization of these parameters, the mixing of already prepared Pd-doped tin oxide powder, the lead glass powder and the available organic binder (ethyl cellulose) is carried out in a ball mill. Mixing is done for one hour using five 10 mm dia zirconia balls. After mixing the organic solvents α-terpineol and Diethyl glycol monobutyl ether acetate are added to powder and the mixture is kept at 80˚C for twenty four hours to get the proper paste. The optimized firing temperature of the paste lies between 750˚C to 800˚C.

Sensitivity of Pd-doped thick film gas sensors

The variation of sensitivity (% change in resistance i.e. $S = \frac{R_a - R_g}{R_a} \times 100$, where R_a and R_g are the resistances of sensor in clean air and in presence of the gas, respectively) with different concentration of ethanol was studied for the fabricated (Pd-doped) SnO_2 sensor, at different fixed temperatures (150^0C-350^0C) and found to maximum sensitivity at 350^0C for ethanol.

3.3 X-ray analysis

The XRD patterns of 1% Pd doped powder are shown in fig.4. Structural analysis was carried out by using X-ray diffractometer (Seifert, Germany, model-ID-3000). The observed pattern has several peaks for different angles. The maxima of peak occur at 26.43^0 in each case. The X-ray diffraction patterns are almost similar and the peak positions in each sample could be indexed with SnO_2 cassiterite structure (JCPDS standard card no. 41-1445). The maxima occur for 110 hkl values. The nature of the XRD pattern does not change with the concentration of Pd. The absence of peaks of Pd in XRD may be due to small amount of Pd. The crystallite size found to be 26.83 nm for 1% Pd doped powder, when calculated from X-ray diffraction pattern using Debye Scherrer formula [9].

$$D = k\frac{\lambda}{\beta \cos\theta}$$

Where D is the mean crystallite diameter, λ is the X-ray wavelength (1.54056Å), k is the Scherrer constant (0.89) and β the full width at half maximum (FWHM) of the diffraction lines.

4. Conclusion

Pd-doped SnO_2 powder has been used to prepare the thick film paste. The developed paste has been screen printed on alumina substrate to realize the thick film gas sensors. SnO_2 sensor was fabricated on a 1″x1″ alumina substrate. It consists of a gas sensitive layer (SnO_2) doped with Pd, a pair of electrodes underneath the gas sensing layer serving as a contact pad for sensor. Also a heater element on the backside of the substrate was printed. The sensitivity of sensor has been studied at different temperatures (150^0C-350^0C) upon exposure to ethanol and found maximum sensitivity for ethanol at 350^0C.

From X-Ray analysis the particle size was found to be 26.83 nm for 1% Pd doped powder.

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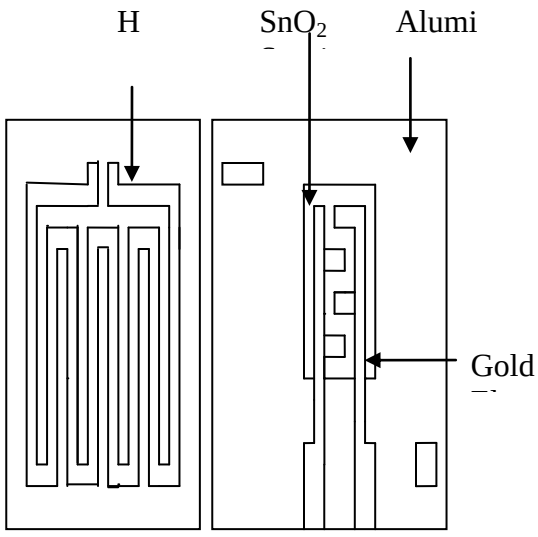

Fig. 1 Schematic of fabricated sensor

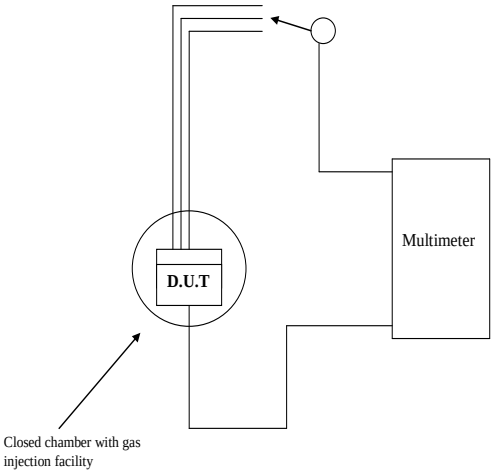

Fig. 2 Schematic diagram of measurement setup

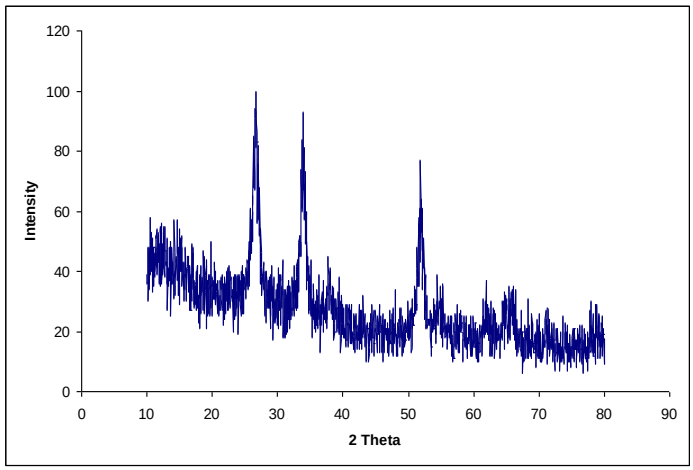

Fig.5 XRD pattern of 1% Pd-doped SnO_2 Thick film Gas Sensor

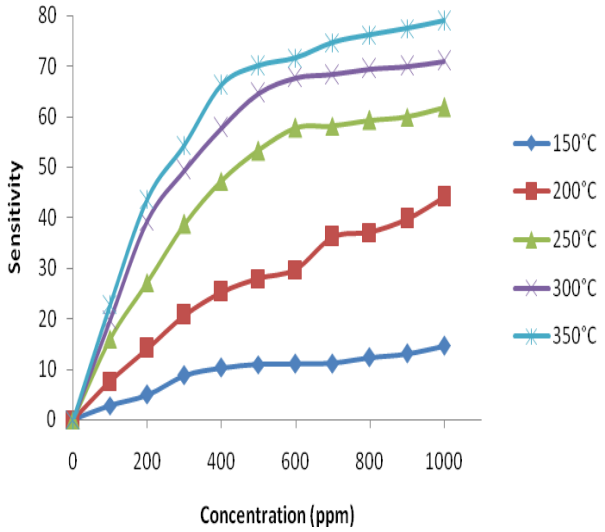

Fig.3 Response of SnO_2 sensor (1%, Pd-doped) on exposure to ethanol at different operating temperature (150^0C-350^0C)