

# ZnO thick film gas sensors fabrication and its structural and electrical Properties

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## ABSTRACT

In the present work, the ZnO thick films were prepared by a standard screen printing method on alumina substrate. The developed thick films were fired at different temperatures in air atmosphere. The structural and electrical properties were investigated. X-Ray diffraction pattern analysis shows that fabricated films are polycrystalline. Scanning electron microscopy SEM shows that the fabricated ZnO films are granular and porous. The DC resistance of the films was measured by half bridge method in air atmosphere at different temperatures. The films were showing decrease in resistance with increase in temperature indicating semiconductor behavior. The resistivity, activation energy and temperature coefficient of resistance (TCR) are evaluated at different firing temperatures.

**Keywords:** Thick film sensor, ZnO, metal oxide thick film, gas sensor

## I. INTRODUCTION

Solid state metal oxide semiconductor gas sensors have proved to be very promising for monitoring the emission of air pollutant and toxic gases because they are a low cost element [1]. Zinc oxide (ZnO) is II-VI compound semiconductor with a wide direct band gap of 3.37eV and a hexagonal structure. ZnO is often used in photovoltaic, gas sensor application, varistors, surface acoustic wave devices, electric transducers, piezoelectric materials and room temperature ultraviolet lasing [2].

There are several deposition methods have been used to grow ZnO films such as spray pyrolysis, vacuum evaporation, chemical vapour deposition, magnetron sputtering, pulsed laser deposition, sol-gel technique, screen printing technique [1-10]. Screen printing technique was introduced in the later part of 1950's to produce compact, robust and relatively inexpensive hybrid circuit for many purposes. Later on thick film

technique has attracted by the sensor field. Screen printing is viable and economical method to produce thick films of various materials [2-3]. The electrical properties of thick films are functions of several factors such as ingredients, manufacturing technique and sintering history. The ingredients of thick film include a conducting paste of an oxide powder, glass frit and an insulating substrate, alumina [4-5].

The present works deals with preparation procedure of ZnO thick films by screen printing technique and study their electrical and structural properties at different firing temperatures.

The experimental work included preparation of thick films of ZnO on alumina substrate by screen printing technique and its structural and electrical characterization. The structural characterization was performed by XRD, SEM and EDAX technique to determine the variation of microstructure, crystallite size, orientation and chemical composition of the

undoped ZnO thick films. Electrical characterization was based on measurement of resistance of the films by half bridge method at different operating temperatures. From measured resistance values, the resistivity, activation energy and TCR were determined. From XRD pattern, different phases and preferred orientation were observed and grain size was determined. SEM indicated the surface morphology of the films and specific surface area was determined. From EDAX, all the films were observed to be non-stoichiometric. For all the undoped films it is observed that resistance decreased with increase in operating temperature indicating semiconducting behavior. The resistivity, activation energy and TCR were observed as a function of operating temperature as well as doping concentration. The prepared films were annealed at various temperature increasing from 650°C to 850°C, then films were oriented more and more preferentially along the (101) direction, the grain size of the ZnO crystal increased.

## II. METHODS AND MATERIAL

### 2.1 ZnO thick film preparation

For undoped ZnO thick film resistors, the inorganic to organic materials ratio was maintained as 80:20 %. In inorganic materials, the commercially available AR grade ZnO powder (AR grade 99.9% pure), was used as a functional material. The ZnO powder was weighed and calcined in air atmosphere at 400°C for 1 h [6]. The ratio of active ZnO powder to permanent binder was kept as 95:5 % in 80 % part. Glass frit was used as a permanent binder. Organic part consists of 10 % ethyl cellulose as a temporary binder and 90 % terpinol as a vehicle to make the paste. Terpinol was added drop by drop to obtain the proper viscosity and thixotropic properties of the paste. The paste was used to prepare thick films on alumina substrate by using standard screen printing technique. After screen printing, the films were dried under IR-lamp for 30 minutes and then fired at temperatures of 650°C, 750°C, 850°C for 2 h in muffle furnace.

### 2.2 Thickness measurement

The thickness of the ZnO thick film was measured by using weight difference method. The thickness of the film was observed in the range of 21 to 25µm.

### 2.3 Structural and morphological Studies

Using X-ray diffraction analysis from 200-800, 2θ was carried out to examine the final compositions of the ZnO thick films samples. The average grain sizes of zinc oxide thick film samples were calculated by using the Scherer formula [6-7],

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad (1)$$

Where D is the average grain size,  $\lambda = 0.1542$  nm (X-ray wavelength), and  $\beta$  is the peak FWHM in radiation and  $\theta$  is diffraction peak position. The surface morphology and chemical composition of the films were analyzed using a Scanning electron microscope SEM. From the SEM photographs, the specific surface area was calculated for spherical particles using the following equation,

$$S_w = \frac{6}{\rho d} \quad (2)$$

Where d is the diameter of the particles,  $\rho$  is the density of the particles.

### 2.4 Electrical characterization

The DC resistance of the films was measured by using half bridge method as a function of temperature. The films were set in a temperature controlled atmosphere. An external resistor  $R_L$  was connected in series with the thick film and fixed DC voltage was applied to the circuit. The values of the film resistance were obtained by measuring output voltage using digital multimeter across the resistor  $R_L$ . Digital temperature controller/monitor system with chromel-alumel thermocouple was used to indicate the operating temperature. The resistivity value of each film was calculated from the dimensions of the film. Activation energy and TCR were evaluated from the observed data in the temperature range 30 – 250°C. The resistance of the thick film ( $R_s$ ) was calculated by the relation,

$$R_s = R_L \left( \frac{V_s}{V_0} - 1 \right) \quad (3)$$

Where

$V_s$  – Applied voltage,

$V_0$  – Voltage across external resistor  $R_L$ .

The Resistivity ( $\rho$ ) of the thick film was calculated by the relation,

$$\rho = \left(\frac{R_s X A}{l}\right) \quad \text{Ohm/m} \quad (4)$$

$$\rho = \left(\frac{R_s X b X t}{l}\right) \quad \text{Ohm/m} \quad (5)$$

Where

$R_s$ = the resistance of thick film.

$l$ = length of the thick film resistor in cm

$t$  = thickness of the film sample

$b$  = breadth of the thick film resistor in cm

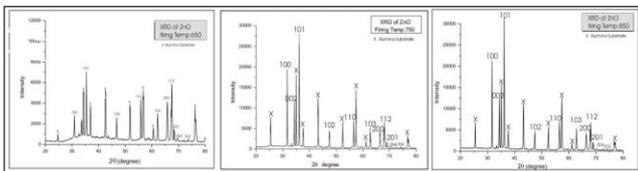
$A$  = cross sectional area of the film resistor  $\text{cm}^2$

$\rho$  = resistivity of thick film resistor in ohm/cm

### III. RESULTS AND DISCUSSION

#### 3.1 X-Ray diffraction analysis

The X-ray diffraction analysis from 200-800 range,  $2\theta$  was carried out using  $\text{CuK}\alpha$  radiation to examine the final compositions of the ZnO thick films samples.

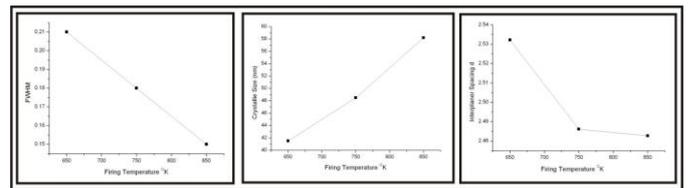


**Figure 1.** X-Ray diffraction pattern of ZnO (a) fired at 650°C (b) fired at 750°C (c) fired at 850°C

The microstructure in thick film of ZnO affected by a various parameters such as the composition, softening point, viscosity, and thermal expansion coefficient and wetting properties of the glass frit, the ratio of the size of glass particles to that of metal oxide grains and the sintering properties of the conductor material are some parameters known to affect the final microstructure of the film.

Figure 1 shows the XRD profiles of the ZnO thick films fired at 650°C, 750°C and 850°C temperatures prepared from AR grade ZnO powder. It is revealed

that all the samples have diffraction peaks corresponding to (100), (002), (101), (102), (110), (103), (200), (112), (201) and (202) directions of the wurtzite hexagonal ZnO crystal structure [JCPDS 36-1451]) similar to A.V. Patil. [8]. some peaks of alumina substrate (indicated with X) was also found in the XRD profile of the ZnO thick film. It has been observed that (101) reflections are of maximum intensity, which indicates that ZnO Thick film resistor have preferred orientation in the (101) plane. The higher peak intensities of an XRD pattern is due to the better crystallinity and bigger grain size can be attributed to the agglomeration of particles. The average crystallite size of ZnO TFRs fired at 650°C, 750°C and 850°C calculated by Scherrer’s formula was observed as 41.494nm, 48.503nm and 58.212nm respectively. And the lattice strain found 0.00287, 0.00241 and 0.00201 respectively.



**Figure 2.** Plot of (a) FWHM, (b) crystallite size and (b) Interplanar spacing  $d$  versus firing temperature (hkl101)

It has been observed that the crystallite size increases with increase in firing temperature. The bigger grain size can be attributed to the agglomeration of particles due to increase in firing temperature [9]. The XRD patterns of all the films seem to be qualitatively similar. Upon increasing the firing temperature from 650°C to 850°C, the  $2\theta$  shifts toward higher value and the FWHM value decreases, indicating that the (101) spacing decreases and the crystallinity (crystalline size) of the ZnO TFR is improved with increasing firing temperature as indicated in Figure 2. These results are thought to be related to the reduction in oxygen atoms due to higher firing temperature.

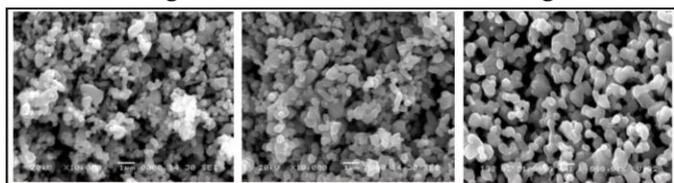
This change influences the stoichiometry of ZnO TFRs. The interplanar spacing of (101) plane is therefore 2.5322, 2.4861 and 2.4827nm for the TFRs

fired at 650, 750, and 850°C respectively Figure 1(c), which is in good agreement with the standard value 2.4759nm shown by JCPDS card 36-1451 file data.

### 3.2 Surface morphology analysis

Scanning electron microscopy is convenient technique to study the microstructure of ZnO thick film samples. A scanning electron microscopy, SEM [Model JOEL 6300(LA) Germany] was employed to characterize the surface morphology. For SEM all the ZnO samples are coated with a very thin conducting gold layer (few100Å) using vacuum evaporation/sputtering technique to avoid charging of the samples.

Figure 3(a), (b) and (c) shows the SEM micrographs of ZnO thick films fired at 650°C, 750°C and 850°C. All the SEM images are recorded at 10000X magnification.



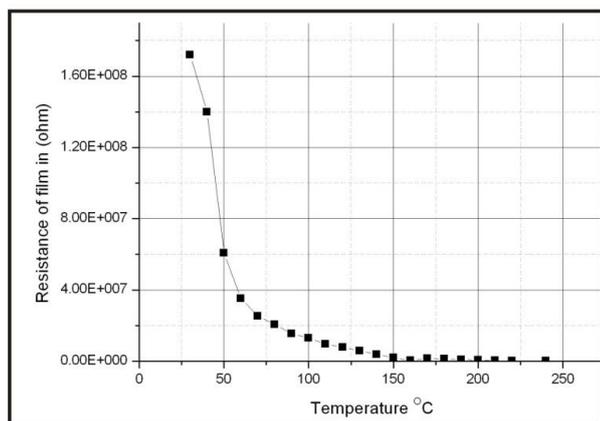
**Figure 3.** SEM Images of ZnO thick film (a) fired at 650°C (b) fired at 750°C (c) Fired at 850°C

Figure 3(a) shows that the film structure is uniform and consists of a large number of spherical grains leading to a high porosity and large effective area available for the adsorption of oxygen species. Figure 3(b) shows that some necks are formed within the structure. Figure 3 (c) shows the strongly agglomerated structure with neck growth. Due to this strong agglomeration, the effective surface-to-volume ratio would be decreased and oxygen adsorption-desorption capability of the film structure would be decreased. The contrast difference is due to the different orientation of the crystallites. It has been observed that an increase in the firing temperature leads to an increase in the particle size and decrease in specific surface area [9-10]. It is thought that the increase in particle size was affected by the promotion of the crystalline phase in the film and neck growth between particles as the firing temperature was

increased. An increase in temperature improves the crystallinity and thus increases the mobility of atoms at the surface of films.

### 3.3 Electrical characteristics

The DC resistances of the films were measured by using half bridge method as a function of temperature [9-10]. Activation energy and TCR were evaluated from the observed data in the temperature range 50-250°C. Resistivity ( $\rho$ ) of the thick film was calculated by the relation [9-10]. Figure 4 shows variation of resistance with temperature for ZnO thick films fired at temperatures 750 °C in air. The plot shows different conduction regions: (i) continuous fall of resistance, (ii) an exponential fall region and (iii) finally saturation region. There is decrease in resistance with increase in temperature, indicating semiconducting behaviour. Any increase in temperature of thick film causes the electrons to acquire enough energy and cross the barrier at grain boundaries. There can be decrease in potential barrier at grain boundaries, since at higher temperatures the oxygen adsorbates are desorbed from the surface of the films. Also at higher temperatures the carrier concentration increases due to intrinsic thermal excitation and electron emission process improves with increase in temperature. The thick film shows decrease in resistance with increase in temperature is due to increasing drift mobility of the charge carriers or due to lattice vibrations associated with increasing temperature, where the atoms occasionally come close enough for the transfer of the charge carriers and the conduction is induced by lattice vibration.



**Figure 4 .** Variation of Resistance with Temperature of ZnO thick films fired at 750°C

#### IV. CONCLUSION

ZnO thick films deposited on alumina substrate using screen printing technique and fired at different temperatures were showing semiconductor behavior. The effect of variation in firing temperature (650-850°C) on the thick films was evaluated. It is found that the films fired at 850 °C offer low resistivity, low activation energy, high TCR and high grain size. XRD and SEM studies have revealed polycrystalline morphology of ZnO thick films. It also shows voids between the particles basically due to evaporation of the organic solvent during the firing of the films. The grain size increases with the firing temperature of the films. The resistance of thick film decreases with increase in surrounding temperature.

#### V. REFERENCES

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