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Effect of firing temperature on electrical and structural characteristics of screen printed ZnO thick films

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ZnO thick films were prepared by using standard screen printing technique and fired at different temperatures in air atmosphere. 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 behaviour.The resistivity, activation energy and temperature coefficient of resistance (TCR) are evaluated at different firing temperatures. The structural behaviour, surface morphology and phase composition were studied by XRD, SEM and EDX technique respectively.

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1. Introduction

ZnO is outstanding semiconductor attracting tremendous attention due to its interesting properties such as wide band gap of 3.37eV at room temperature with large exciton binding energy (60meV), high chemical stability, low dielectric constant, large electrochemical coupling coefficient and high luminous transmittance [1]. It is widely used in photovoltaic, gas sensor application, varistors, surface acoustic wave devices, electric transducers, piezoelectric materials and room temperature ultraviolet lasing [2, 3]. Therefore it can be applied extensively to IT (Information tech.), BT (Bio-tech.), ET (Environmental tech.)[4]. Several deposition methods have been used to grow undoped and doped ZnO films such as Spray pyrolysis,Vaccum evaporation, chemical vapour deposition, magnetron sputtering, pulsed laser deposition, sol-gel technique, screen printing technique[5]. 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 [6]. Screen printing is viable and economical method to produce thick films of various materials [7-14].

ZnO is II-VI semiconductor. Its resistivity can be controlled by the deposition process to sufficiently low value. Its electrical conductivity is mainly due to Zinc excess at interstitial position. The electrical properties of thick films are functions of several factors [15] such as ingredients, manufacturing technique and sintering history. The ingredients of thick film include a conducting paste of an oxide powder, glass firit and an insulating substrate, alumina.

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.

2. Experimental

2.1 Powder and paste preparation

The ZnO powder (AR grade, 99.99%) was weighed and calcined in air at 400^0C for 2 h. The calcined ZnO powder was crushed and mixed thoroughly with glass frit as permanent binder and ethyl cellulose as a temporary binder. The mixture was then mixed with butyl carbitol acetate as a vehicle to make the paste.

2.2 Thick film preparation

Fig. 1 shows the process sequence diagram for preparation of ZnO thick films. The paste was used to prepare thick films on alumina substrate by using standard screen printing technique using 140s mesh no. 355. After screen printing, the films were dried under IR-lamp for 60 minutes and then fired at temperatures of 700^0C, 800^0C, 900^0C for 2 h in muffle furnace.

2.3 Thickness measurements

The thickness of the ZnO thick films was measured by using Taylor-Hobson (Taly-step UK) system. The thickness of the films was observed uniform in the range of 20μm to 22μm

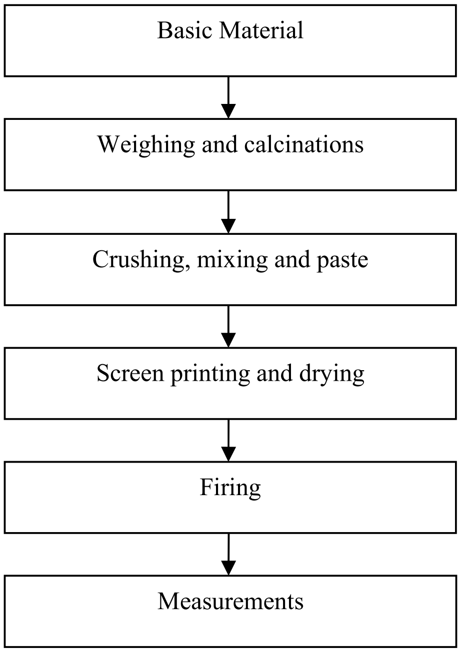


Fig. 1. Process sequence for thick film preparation.

2.4 Electrical characterization

The DC resistance of the films was measured by using half bridge method as a function of temperature described elsewhere [16, 17]. 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 (classic 5175 DM, $\pm$0.5%) across the resistor R_L.Digital temperature controller/monitor system with chromel-alumel thermocouple was used to indicate the operating temperature. The resistance of the thick film (Rs) was calculated by the relation,

$$R_S = R_L\left(\frac{V_{app}}{V_o} - 1\right) \tag{1}$$

where Vapp – Applied voltage Vo – Voltage across external resistor RL.

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 40 - 250 °C.

2.5 Structural and morphological Studies

Using X-ray diffraction (Miniflex Model, Rigaku, Japan) analysis from 20-80^0, 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 Debye- Scherrer formula [18],

$$D = \frac{0.9\lambda}{\beta\cos\theta} \tag{2}$$

where D is the average grain size, λ =0.1542 nm (X-ray wavelength), and β is the peak FWHM in radiation and θ is diffraction peak position. The surface morphology and chemical composition of the films were analyzed using a Scanning electron microscope [SEM model JEOL 6300 (LA) Germany] coupled with an energy dispersive spectrometer (EDS JEOL, JED-2300, Germany).

The details of preparation, XRD information and grain size of the films are given in Table 1.

Table 1. Details of the preparation and XRD information of ZnO thick films.

1	Material	Zinc Oxide (AR Grade)
2	Substrate material	Alumina
3	Deposition technique	Screen printing method
4	Type of screen used	140s-mesh no.355
5	Settling time	10 min.
6	Drying under IR time	60 min.
7	Firing time	2 h
8	Peak firing temperature	700,800,900 °C
9	XRD details	Rigaku diffractometer, Miniflex model Japan
10	SEM and EDX detail	JEOL6300 (LA) with JED-2300, Germany

3. Results and discussions

3.1 X-Ray diffraction analysis

In order to understand the structural properties of ZnO film samples fired at different temperatures in air atmosphere, the X-ray diffraction study was undertaken. X-ray diffraction analysis of ZnO film samples were carried out in the 20-80^0 range using Cuk_α radiation. Figure.2 shows an XRD pattern of ZnO film samples plotted in the range 20-80^0 (2θ) verses intensity having several peaks of zinc oxide indicating random orientation for the polycrystalline nature and measured interplaner distances agreed with the values reported for ZnO in the literature. The observed peaks match well with the reported ASTM data of Zinc oxide, confirming the polycrystalline nature. 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 was calculated using Scherrer equation and was estimated to be about 18.64nm, 24.79nm, and 37.23nm for 700^{0}C, 800^{0}C, 900^{0}C respectively.

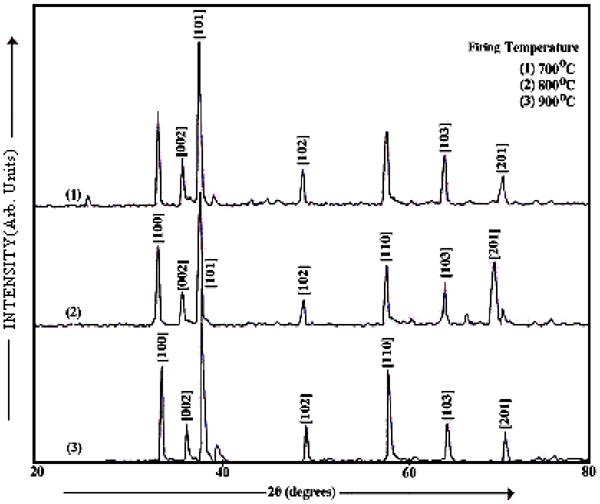


Fig. 2. XRD pattern of ZnO thick films fired at 700^{0}C, 800^{0}C, 900^{0}C.

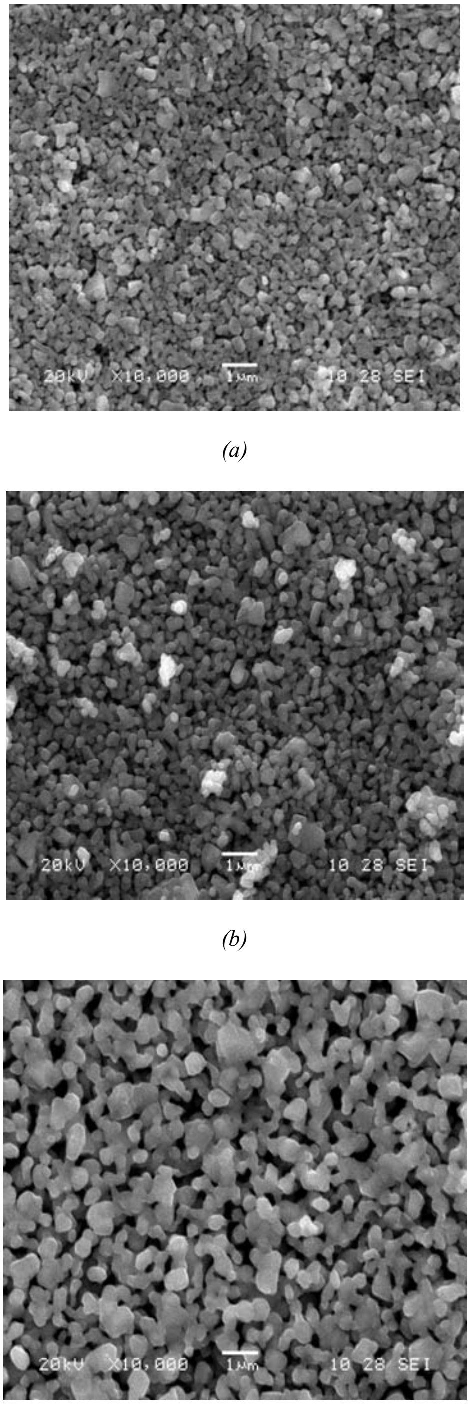
3.2 Surface morphology analysis

Fig. 3 shows SEM images of ZnO thick film fired at 700^{o}C, 800^{o}C, 900^{o}C. Micro structural chacterization was carried out by using scanning electron microscopy. SEM indicated that the microstructure is nearly uniform with negligible open porosity. However presence of some residual, intragranular porosity was seen. It is found that the grain size and the crystalline quality increased with increase in firing temperature. The firing increases the atomic mobility; the atoms can be moved to more energetically favoured sites such as voids, grain boundaries and interstitial positions. An increase in temperature improves the crystallinity and thus increases the mobility of atoms at the surface of films. The film fired at 700^{o}C has good adhesion. Therefore it is used for further application work.

3.3 Elemental analysis

The composition of ZnO thick films fired at different temperatures was analyzed by energy dispersive spectrometer (6360LA) (EDX). Table 2 shows the composition of the films fired at different temperatures.

The EDX spectrum showed the presence of only Zn and Oxygen. The mass percentage of oxygen was found to decrease with increasing firing temperature due to release of excess oxygen [19]. From the analysis it was found that ZnO films are non- stoichiometric.



(a)

(b)

(c)

Fig. 3. SEM images for ZnO film at firing temperatures (a) 700^{0}C, (b) 800^0 C, (c) 900^0 C.

Table 2. Composition of the films at different firing temperature.

Firing temperature	Element	At.Wt. %	Mass %
700 °C	Zn O	80.39 19.61	94.37 5.63
800 °C	Zn O	82.66 17.34	95.12 4.88
900 °C	Zn O	83.47 16.53	95.38 4.62

3.4 Electrical characteristics

Fig. 4 shows variation of resistance with Temperature for ZnO thick films fired at temperatures 700,800,900 °C respectively 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 boundries [20,21]. There can be decrease in potential barrier at grain boundries, since at higher temperatures the oxygen adsorbates are desorbed from the surface of the films [20, 22].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 [20, 23]

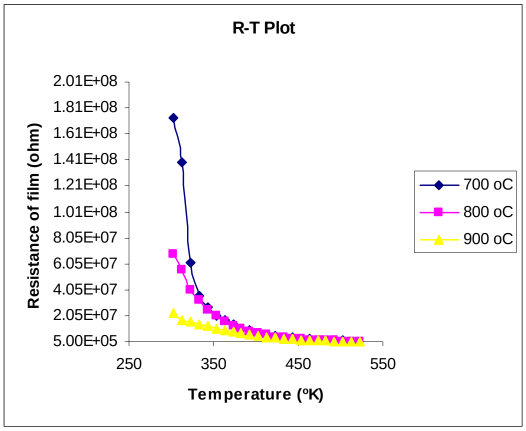


Fig. 4. Variation of resistance with temperature of ZnO thick films fired at 700,800,900 °C.

Fig. 5 shows Arrhenius plot of Log Rs versus 1/T for ZnO thick films. The activation energy in the low temperature region is always less than the energy in the high temperature region because material passes from one conduction mechanism to another [24].In the low temperature region ,the increase in conductivity is due to the mobility of charge carrier, which is depend on the defects/dislocation concentration. So the conduction mechanism is usually called the region of low temperature conduction. In this region activation energy decreases because a small thermal energies quite sufficient for the activation of charge carriers to take part in the conduction process. In the other words the vacancies/defects weakly attached in the lattice can easily migrate. Hence increase in conductivity in the lower temperature region can be attributed to the increase of charge mobility.

In high temperature region, the activation energy is higher than that of low temperature region. In this region the electrical conductivity is mainly determined by the intrinsic defects and hence is called as intrinsic conduction. The high values of activation energy in this region may be attributed to the the fact that the energy needed to form the defects is much larger than the energy required for its drift. That is why the intrinsic defects caused by the thermal fluctuations determine the electrical conductance of the films only at elevated temperature. [24, 25].

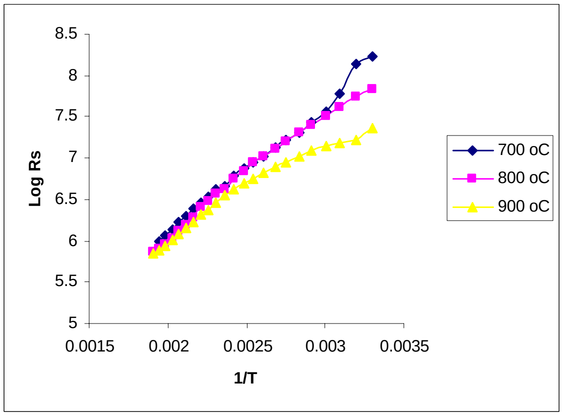


Fig. 5. Plot of Log Rs Vs 1/T of ZnO thick films fired at 700,800,900 °C.

The variation of grain size, resistivity, TCR and activation energies of ZnO thick films with firing temperature is summarized in Table 3. It is observed that the resistivity, activation energy decreases where as TCR and grain size increases with increasing firing temperature. These results may be attributed to increase in the degree of crystallinity with the firing temperature.

Table 3. Grain size, resistivity, TCR and activation energy of ZnO thick films fired at different temperatures.

Firing Temp. ^{o}C	Grain Size, nm	TCR (/^{o}C) At const. temp	Resistivity (Ω m)	Activation energy (eV) L.T Region	H.T. Region
700	18.64	1.41×10^{-3}	2.288×10^{3}	0.2683	0.3508
800	24.79	3.09×10^{-3}	0.898×10^{3}	0.2444	0.3404
900	37.23	6.52×10^{-3}	0.305×10^{3}	0.1414	0.2116

4. Conclusions

ZnO thick films deposited on alumina substrate using screen printing technique and fired at different temperatures were showing semiconductor behaviour. The effect of variation in firing temperature (700-900 ^{o}C) on the thick films was evaluated. It is found that the films fired at 900 ^{o}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.

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