Structural Characterization of ZnO Thick Films Annealed at Different Temperatures

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ABSTRACT

The ZnO powder was synthesized by self-propagating solution combustion method at 430^{0}C. XRD of powder confirms the formation of zinc oxide. The thick film of synthesised ZnO powder were prepared by screen printing method and annealed at 500^{0}C, 600^{0}C and 700^{0}C temperatures in muffle furnace. The structural characterization of films was studied using XRD and SEM. The presence of diffraction peaks in XRD indicates that the films were polycrystalline with a hexagonal wurtzite type crystal structure. Microstructure shows that some necks are formed within the structure.

Keywords: ZnO, self-propagating, thick film, XRD, SEM.

INTRODUCTION

Zinc oxide is widely used material in world wide. Because of high bandwidth it shows sensitivity to many gases and widely used in all type of applications[1]. There are different method to synthesize zinc oxide powder like chemical precipitation method, flame spray pyrolysis, vapour deposition, oxidation, sputtering, and pulse laser deposition, gel combustion method etc. Each method has there advantages and disadvantages. In a gel combustion method an oxidizing agent usually nitrate and a fuel as a reducing agent are used. Gel combustion gives homogeneous, high purity, and high quality nano-powders[2]. Here ZnO powder was prepared by a gel combustion method using Zinc nitrate and dextrose as a fuel [3].The prepared powder was used to form thick films. Screen printing method was used to prepared thick films and it structural characteristic was studied using XRD and SEM.

EXPERIMENTAL PROCEDURE

The 1.35M zinc nitrate hexahydrate and 0.79 M dextrose was dissolved in water and heated to form a gel like structured. Then the solution was kept in preheated muffle furnace at 430^{0}C for combustion and the powder was prepared. The powder was sintered at 600^{0}C to get nanocrystalline ZnO powder. The formation of ZnO powder was confirmed by XRD. Screen printing is a viable and economical method to produce thick films of various materials which has been used to produce varistors, actuators, sensor, solar cells etc. Screen printing method is simple, low cost, fast and high reproducibility. The ZnO thick films on alumina substrate were prepared using screen printing method. A thick film paste was prepared by adding suitable binder and solvent. After screen printing the films were dried under IR-lamp for 60 minutes and then annealed at temperatures of 500, 600 and 700^{o}C for 2hr firing cycle in muffle furnace. 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 35μm.

RESULT AND DISCUSSION

XRD characterization

XRD for synthesized ZnO Powder

X-ray diffraction technique was used to determine the crystalline structure and preferential orientation of the crystallites materials and also to calculate the crystallite size[4]. For a synthesized ZnO powder and thick films low angle XRD was used. X-ray generator [Miniflex Model, Japan] Rigaku diffractometer (DMAX-500) was employed. The XRD of synthesize powder confirms the formation of ZnO powder as shown in fig.(1) [JCPDS card 36-1451 file data].The average crystallite sized of synthesized powder was 29.98nm calculated using Scherer's formula.

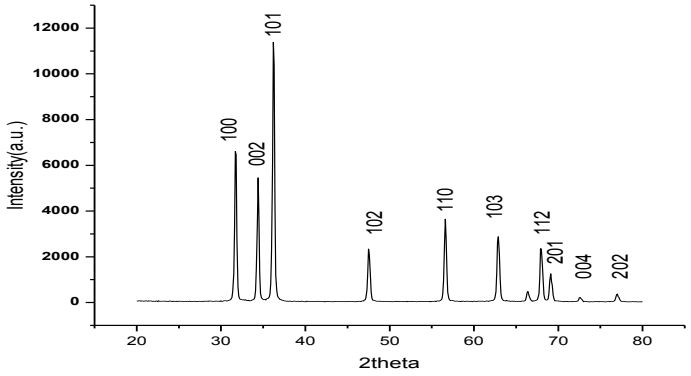


Fig. 1: XRD pattern of synthesized ZnO powder at temperature 430^{0}C.

XRD for Screen printed ZnO thick films annealed at different temperatures

The XRD patterns of prepared screen printed thick films were shown in fig. 2 (a), (b) and (c).

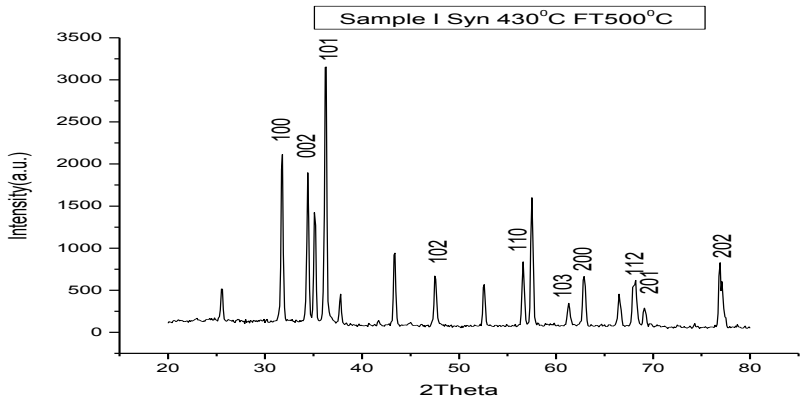


Fig. 2 (a) : Annealed at 500^{0}C

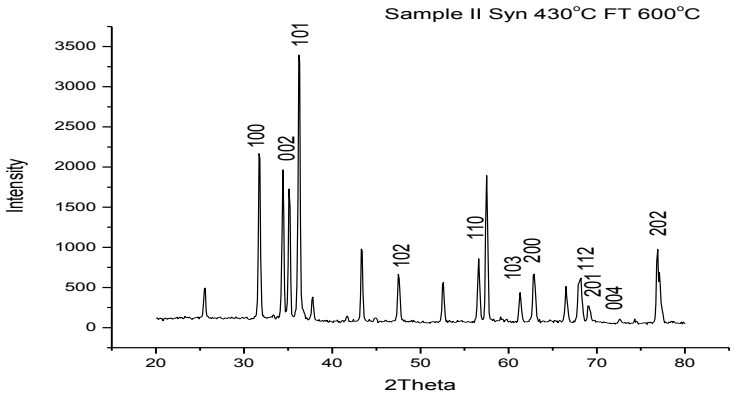


Fig. 2 (b): Annealed at 600^0C

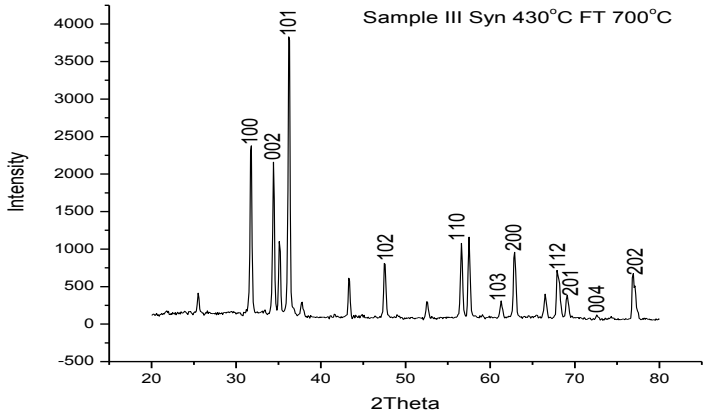


Fig. 2 (c): Annealed at 700^0C

Fig: 2: XRD pattern of ZnO thick films annealed at different temperature

All the samples have peaks corresponding to (100), (002), (101), (102), (110), (103) and (112) directions of the hexagonal ZnO crystal structure similar to Joseph et al.[5]. It shows that all the samples have a preferred growth orientation along c-axis i.e. (101) plane, the peak intensity of which increases with increase in firing temperature of the film. Crystalline nature increases as firing temperature increased to 700°C. The other peaks observed correspond to the alumina substrate. The increase in Zn content and annealed temperature is the reason for high preferential orientation along the (101) plane.

The crystallite size was determined using Scherer's formula:

$$D = 0.94\lambda/\beta\cos\theta$$

The variation of crystallite size with firing temperature is indicated in table1.

Table1: Variation of crystallite size with firing temperature

Firing Temp. in deg. (Syn.Temp.400)	**Crystallite size(nm) (101)**
500	27.71
600	27.96
700	34.13

The bigger grain size can be attributed to the agglomeration of particles due to increase in firing temperature. The effect of the firing temperature on the orientation of the films was investigated by calculating the texture coefficient using the following equation [6,7 and 8].

$$T_{C(hkl)} = \frac{I_{(hkl)}/I_{O(hkl)}}{1/N[\sum_N I_{(hkl)}/I_{O(hkl)}]}$$

where $h_{(hkl)}$ = Texture coefficient of the (hkl) plane
$I_{(hkl)}$ = Measured intensity,
$Io_{(hkl)}$ = JCPDS standard intensity and
N = Number of diffraction peaks

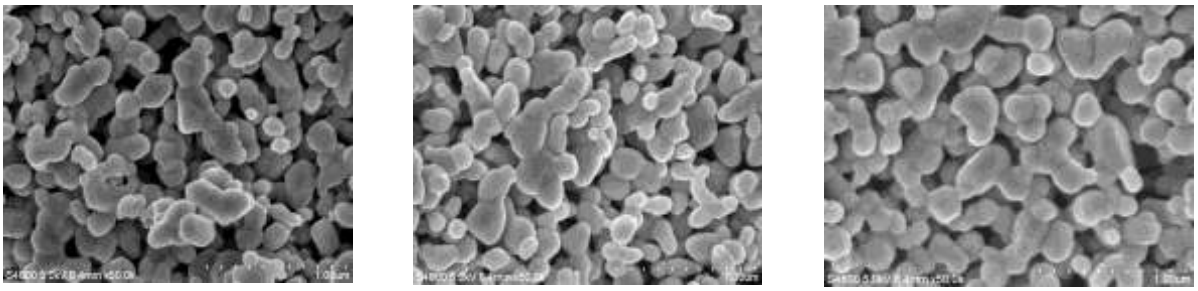
It was observed that T_C is larger than unity for a preferentially oriented (hkl) plane [9,10]. The lower values of T_C reveals that the films have poor crystallinity and this may be improved at a higher firing temperature.

Table 2: Effect of firing temperature on orientation of the films

Synthesis temp.(^{0}C)	Firing temp. (^{0}C)	Texture coefficient		
		(100)	(002)	(101)
400	500	1.828	1.6399	2.7317
	600	1.8956	1.7082	2.9263
	700	1.9177	1.74496	3.0876

Scanning electron microscopy of screen printed ZnO thick films

Scanning electron microscopy is convenient technique to study the microstructure of thick film samples. The scanning electron microscopy, SEM [Model JOEL 6300(LA) Germany] was employed to characterize the surface morphology of synthesized ZnO thick films as shown in fig 3.It showed that the particles are randomly oriented with some holes indicating porosity is present.



(a) annealed temp 500 ^{0}C (b) annealed temp 600 ^{0}C (c) annealed temp 700 ^{0}C

Fig. 3: SEM image of ZnO thick films showing decreased porosity and increased average grain size as annealed temperature is increased from 500^{0}C to 700^{0}C.

A high surface area facilitates the chemisorptions process by increasing the adsorption and desorption rates. The specific surface area of ZnO thick films was calculated using BET method using the following equation [14].

$$S_w = 6/\rho d$$

An increase in the firing temperature leads to an increase in the particle size and decrease in specific surface area [11,12 and 13]as shown in table 3. Which decreases the sensitivity towards the gas sensing.

Table 3: Particle size and specific surface area determined from SEM

Firing temp.	Particle Size, d µm(SEM)	Specific surface Area in m^2/g
500	1.25	0.855615
600	2.25	0.475342
700	2.38	0.449378

The porosity was decreased, the particle sizes increases and the surface roughness increases with increasing annealed temperature.

CONCLUSION

It is possible to synthesize the nano powder using self-propagating solution combustion method at high temperature. The screen printed thick film samples shows the high crystalline nature. The specific surface area decreases as the firing temperature increased which results poor sensitivity.

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