

Studies on Physical and Electrical Characterization of Al₂O₃-ZnO Composite Material and its Thick Films

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Abstract: Al₂O₃ - ZnO composite material was obtained by adding the Aluminium chloride (AlCl₃ · 6H₂O) (Hexahydrate) powder of different weight percent (0.5, 1.3, 5 and 7 wt %) and Analar Reagent grade (99.9 % pure) ZnO powder by mixing mechanochemically in acetone medium. The prepared materials were sintered at 1000°C for 12h in air ambience and ball milled to ensure sufficiently fine particle size. The structural properties of the powder materials were investigated by X-ray diffraction analysis. The observed powder materials show the polycrystalline nature and the crystallite size found to be in the range of 10 to 36 nm. The thick films of undoped ZnO and Al₂O₃ doped-ZnO were prepared by screen printing technique. The surface morphology of the films was studied by SEM and it shows the films are porous in nature and petal-shaped grains of sizes varies from 190nm to 276nm were observed. The final composition of each film was determined by EDAX analysis. The At. wt. % of Zn and O in each sample was not as per stoichiometric proportion. The electrical conductivity and activation energy of all films were determined.

Keywords: ZnO, Al₂O₃, Thick Films, Crystalline size, Electrical Conductivity, Activation Energy.

1. Introduction

The requirements of semiconductor material are increased along with the expanding of global electronic industry [1] [2]. Semiconductor metal oxides as high performance catalysts for energetically and environmentally improved catalytic combustion of sulfur and hydrocarbons. In order to enhance the catalytic activity (oxidation), the oxides were doped with it using mechanical mixing of some impurities. The aim of present research work is to enhance the catalytic activity (oxidation) of Zinc Oxide (ZnO) using mechanical mixing of Al₂O₃. Metal oxides are extremely important technological materials for use in electronic and photonic devices. The conventional oxide-mixing techniques; powders are produced more homogeneous after the sintering process. In addition, the grain size obtained is much smaller [3]-[4].

Al₂O₃ is weak n-type semiconductor material with wide band gap(8.8 eV) for bulk material in different crystalline form and good thermal stability. It works as good catalyst with semiconductor when the gases such as H₂S and Ethanol come in contact with it.

Zinc oxide (ZnO) is an n-type direct band semiconductor of a wide bandgap (3.4 eV). It is an important multifunctional material with wide ranging applications in varistors [5], surface acoustic wave (SAW) devices [6], transparent conducting oxide electrodes [7], solar cells [8], blue/UV light emitting devices [9], gas sensors [10]-[11], etc. Its conductivity can be tailored by controlling the deviation from stoichiometry and by doping [12]. The undoped -ZnO has high n-type conductivity due to defects such as oxygen vacancies and Zn interstitials, which form donor levels [13]. Group IIIa elements (Al, Ga, In) have been used to improve the electrical conductivity and thermal stability of ZnO films. For this work, Al³⁺ substitution on Zn²⁺ was chosen due to the small ion size of Al³⁺ compared to that of Zn²⁺ (Al³⁺ (0.53Å) and Zn²⁺ (0.74 Å)).

2. Experimental Procedure

2.1 Preparation of Functional Material

Al₂O₃ - ZnO composite material were obtained by adding the Aluminium chloride (AlCl₃ · 6H₂O) (Hexahydrate) powder of different weight percent (0.5, 1.3, 5 and 7 wt %) and Analar Reagent grade (99.9 % pure) ZnO powder by mixing mechanochemically in acetone medium. The prepared materials were sintered at 1000°C for 12h in air ambience and ball milled to ensure sufficiently fine particle size.

2.2. Preparation of Thick Films

The thixotropic paste was formulated by mixing the fine powder of functional material with a solution of ethyl cellulose (a temporary binder) [14] in a mixture of organic solvents such as butyl cellulose, butyl carbitol acetate and terpineol, etc. The ratio of the inorganic to organic part was kept at 75:25 in formulating the paste. This paste was screen-printed [15]-[16] on a glass substrate in a desired pattern (1.5cm x 0.5cm). The films were fired at 550°C for 30 min. in air atmosphere

2.3. Thickness measurements of films

The range of thicknesses of the films was observed in the range from 55 to 65µm. The reproducibility in thickness of the films was possible by maintaining the proper rheology and thixotropy of the paste.

3. Physical Characterization

3.1. Structural analysis

In order to understand the structural properties of Al₂O₃ - doped ZnO powder materials at different dopant concentration, X-ray diffraction analysis of these sintered

powders were carried out in the 20-80° range using CuK_α radiation.

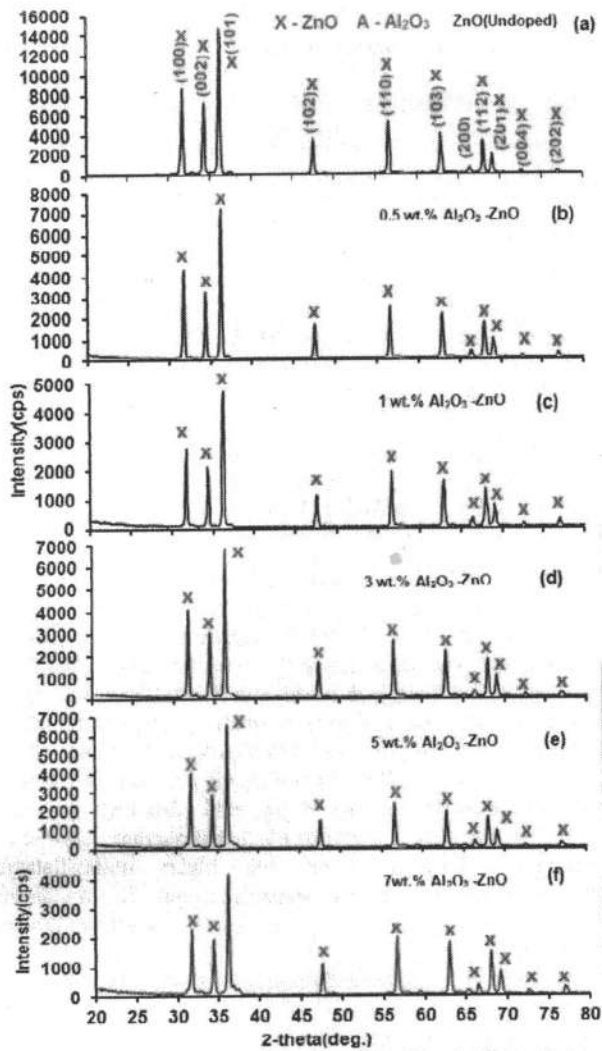


Figure 1: XRD pattern of undoped ZnO and Al₂O₃-ZnO composite material

Figs.1 (a - f) shows XRD patterns of undoped- ZnO, Al₂O₃ and Al₂O₃-ZnO (0.5, 1, 3, 5 and 7 wt. %). Fig.1 (a) shows XRD patterns of ZnO material. The observed diffraction peaks of ZnO are corresponding to the hexagonal wurtzite structure of ZnO. The observed peaks are well matched with the JCPDS (76-0704) reported data of ZnO. The sharp peaks of XRD are corresponds to ZnO material and are observed to be polycrystalline in nature. The higher peak intensities of an XRD pattern is due to the better crystallinity with preferred orientation along the (101) direction.

Figs. 1(b-f) show the XRD patterns of 0.5, 1, 3.5, and 7 wt. % Al₂O₃-ZnO. For all the compositions, formation of only ZnO wurtzite phase is observed in accordance with the reported d-values (JCPDS 76-0704). In corresponding XRD data of such materials, the observed diffraction peaks correspond to the hexagonal wurtzite structure of ZnO (JCPDS 76-0704). The higher peak intensities of an XRD pattern are due to the better crystallinity.

Fig.1 shows the XRD spectra of Al₂O₃-doped ZnO composite material. All the patterns exhibit an intensive (002) XRD peak, indicating that they have c-axis-preferred orientation due to the self-texturing mechanism as discussed by Deng et al [23]. The 2θ values of the diffraction peaks (002) are located at 34.40°, which are very close to that of standard ZnO crystal. No Al₂O₃ or ZnAl₂O₄ phase was detected from the XRD spectra. This may be due to aluminum replacing zinc substitutionally in the hexagonal lattice or aluminum segregating to the noncrystalline region in grain boundary.

From the XRD results, it is concluded that the material properties are strongly dependent on aluminum concentration. The diffraction peak intensity of Al₂O₃:ZnO films decreased with increased doping concentrations. This indicates that an increase in doping concentration deteriorates the crystallinity of the films, which may be due to the formation of the stresses by the difference in ion sizes between zinc and the dopant [17, 18] and the segregation of dopants in grain boundaries for high doping concentrations.

The average crystallite size was calculated from XRD pattern using Debye Scherer's formula [19].

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

Where D- is average crystallite size,
 β - is the broadening of the diffraction line measured at half maximum intensity(FWHM),
 λ-is wavelength of the x- ray radiation and (0.1542 nm).
 θ - is the Bragg angle

Table 1: XRD data of of undoped ZnO and Al₂O₃-ZnO composite material

Sample	Sr. No.	2θ deg.	d- (Å)	FWHM	D(nm)	Plane (hkl)
Undoped ZnO	1	31.70	2.82	0.265	35	Z-100
	2	72.60	1.30	0.427	26	Z-004
0.5 wt.% Al ₂ O ₃ -ZnO	1	31.80	2.81	0.259	35	Z-100
	2	72.60	1.29	1.112	10	Z-004
1 wt.% Al ₂ O ₃ -ZnO	1	31.80	2.80	0.258	36	Z-100
	2	72.60	1.30	0.584	19	Z-004
3 wt.% Al ₂ O ₃ -ZnO	1	31.80	2.81	0.259	35	Z-100
	2	72.60	1.30	0.611	18	Z-004
5 wt.% Al ₂ O ₃ -ZnO	1	31.80	2.80	0.259	35	Z-100
	2	72.60	1.30	1.112	10	Z-004
7 wt.% Al ₂ O ₃ -ZnO	1	31.80	2.81	0.259	35	Z-100
	2	72.60	1.298	1.112	10	Z-004

d = Interplaner distance in Å
 D = Crystallite Size in nm

Table 1 shows the variation of crystallite size with doping concentration of Al₂O₃ in ZnO samples. Slightly broadening of diffraction lines may be attributed to small crystalline effects [20]. From the XRD pattern, the lattice constants of hexagonal ZnO phase can be calculated using the equation [20]-[21].

$$\frac{1}{d_{(hkl)}^2} = \left(\frac{4}{3}\right) \times \left(\frac{h^2+hk+k^2}{a^2}\right) + \left(\frac{l^2}{c^2}\right) \quad (2)$$

$$\frac{c}{a} = \sqrt{\frac{8}{3}} \quad (3)$$

Where d - is interplanar distance,
 a and c - are lattice constants (hexagonal structure)

Table 2: Lattice constants Al₂O₃-doped ZnO composite material

Phase	hkl-Plane	2θ	d (Å)	a (Å)	c (Å)
ZnO (Undoped)	101	36.20	2.4794	3.240	5.291
0.5 wt.% Al ₂ O ₃ -ZnO	101	36.20	2.4720	3.231	5.276
1 wt.% Al ₂ O ₃ -ZnO	101	36.20	2.4688	3.226	5.269
3 wt.% Al ₂ O ₃ -ZnO	101	36.20	2.4753	3.235	5.283
5 wt.% Al ₂ O ₃ -ZnO	101	36.20	2.4720	3.231	5.276
7 wt.% Al ₂ O ₃ -ZnO	101	36.20	2.4720	3.231	5.276

From Table 2, it has been observed that there is variation of lattice constants from JCPDS value (a = 3.253Å, c = 5.213Å). The ionic radius of Zn²⁺ is 0.74Å and of Al³⁺ is 0.53Å [22]. This should result in decreased lattice parameters as per Vegard's Law. However, such a trend is not observed as the sintering temperature is very low, and hence diffusion of Al into Zn sites might not have occurred to a complete extent. The possible formation of Al₂O₃ or ZnAl₂O₄ phases was not detected. This might be due to relatively low sintering temperature (~1000°C) at which their crystallization might not have occurred, suggesting formation of the secondary phases probably in the amorphous form.

3.2. Micro structural analysis of the films

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 X-ray analysis. (EDAX, JEOL, JED-2300, Germany). Figs. 2 (a-e) show the surface morphology of thick films of pure ZnO and Al₂O₃-ZnO (0.5, 1, 3.5, and 7 wt. %) thick films. Plane-view SEM investigation reveals a porous structure of the ZnO films with different Al₂O₃ doping concentrations. Petal-shaped grains of various sizes were observed in all samples. The grains of sizes varies from 190nm to 276nm. The majority of these grains appear several times larger than the average crystallite sizes calculated from X-ray diffraction data (10-36 nm) thus, indicating that most of the grains comprise multiple crystallites. No systematic variation in the microstructure of the ZnO films as a function of the doping concentration was detected.

The ZnO film doped with 1 wt. % Al₂O₃ was observed to be the most porous. The Al₂O₃ additives would present on the ZnO grains are in an optimum level leading to high porosity..

In Figs.2 (d, e and f), the Al₂O₃ additives distributed on ZnO grains would be greater than optimum level, it reduces the porosity of the film surface.

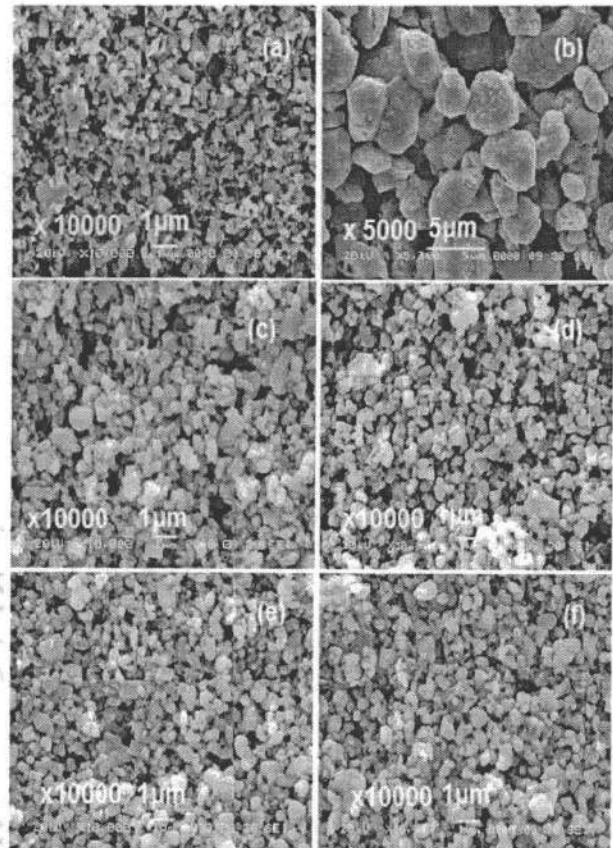


Figure 2: SEM images of (a) undoped ZnO, (b) 0.5 wt.% Al₂O₃-ZnO, (c) 1 wt.% Al₂O₃-ZnO, (d) 3 wt.% Al₂O₃-ZnO, (e) 5 wt.% Al₂O₃-ZnO, and (f) 7 wt.% Al₂O₃-ZnO films

3.3 Elemental analysis of the films

The composition of pure and Al₂O₃-doped ZnO thick films with different mass ratio were analyzed by energy dispersive X-ray analysis. ((EDAX, 6360LA).

Table 3: Quantitative elemental analysis of undoped ZnO and Al₂O₃-ZnO films

Sample	At. Wt. % of Elements			
	O	Zn	Al	Total
ZnO (Undoped)	21.18	78.82	-	100
0.5 wt.% Al ₂ O ₃ -ZnO	16.71	83.44	0.35	100
1 wt.% Al ₂ O ₃ -ZnO	15.43	83.45	2.12	100
3 wt.% Al ₂ O ₃ -ZnO	17.25	80.22	2.53	100
5 wt.% Al ₂ O ₃ -ZnO	18.31	77.83	3.86	100
7 wt.% Al ₂ O ₃ -ZnO	18.44	76.28	5.27	100

Table.3 gives quantitative elemental analysis of Al₂O₃-doped ZnO thick films at different level. The EDAX analysis shows presence of only Zn, Al and O as expected, no other impurity elements were present in the thick films. The EDAX result shows variation in Zn/O ratio and Al/Zn ratio with variation in doping concentration. The At. wt. % of Zn and O in each sample was not as per stoichiometric proportion. The entire samples were observed to be oxygen deficient.

Table 7.4: Activation energy of undoped and Al₂O₃ -ZnO film with temperature

T(°C)	Activation energy (ev)					
	Undoped ZnO	Al ₂ O ₃ -doped ZnO				
		0.5wt.%	1%wt.	3%wt.	5%wt.	7wt%
100	0.032	0.076	0.031	0.007	0.067	0.028
150	0.028	0.092	0.023	0.005	0.080	0.053
200	0.011	0.094	0.028	0.004	0.078	0.061
250	0.024	0.092	0.026	0.002	0.071	0.071
300	0.064	0.087	0.011	0.005	0.045	0.086
350	0.100	0.070	0.007	0.028	0.004	0.102
400	0.139	0.051	0.003	0.076	0.017	0.116
450	0.177	0.026	0.052	0.086	0.025	0.130

Table 7.4 shows the calculated activation energy of all samples for different doping concentration at different operating temperature regions. Fig. 7.5 shows variation of activation energy of undoped and Al₂O₃ doped ZnO thick films as the function of operating temperature.

The graph shows that the doped film having low activation energy than undoped film. It also shows that the activation energy varies with the dopant concentration. The film doped with 3 wt. % of Al₂O₃ shows lowest activation energy than other doping concentrations. It may be due the barrier height decreases as Al₂O₃ doping increases..

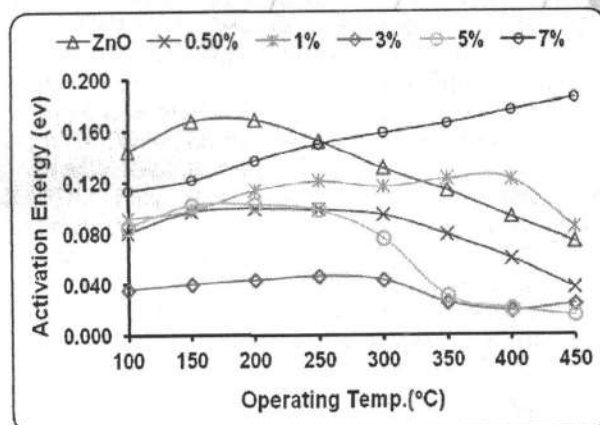


Figure 5: Variation of activation energy with temperature of undoped and Al₂O₃ - ZnO films

5. Summary and Conclusions

From the results obtained, following conclusions can be made

- 1) It shows that the Al₂O₃ -ZnO functional material can be obtained by mechanochemical method.
- 2) The XRD analysis shows that the observed powder materials show the polycrystalline nature and the variation in the crystallite size due to doping. The crystallite size was found to be in the range of 10 to 36 nm.
- 3) The SEM analysis shows the surface morphology of the of undoped ZnO and Al₂O₃ doped-ZnO thick films and it shows the films are porous in nature and petal-shaped grains oriented randomly of sizes varies from 190nm to 276nm were observed.

- 4) The EDAX analysis shows final composition of each film. The At. wt. % of Zn and O in each sample was not as per stoichiometric proportion. The entire samples were observed to be oxygen deficient.
- 5) The electrical conductivity for 0.5, 1, 3 wt. % Al₂O₃ doped ZnO increase while at higher dopant concentrations of Al₂O₃ (5, 7 wt. %) it decrease.
- 6) The doped film shows low activation energy than undoped film. It also shows that the activation energy varies with the dopant concentration. The film doped with 3 wt. % of Al₂O₃ shows lowest activation energy than other doping concentrations. It may be due the barrier height decreases as Al₂O₃ doping increases.
- 7) Al₂O₃ doped-ZnO thick films would be use full for gas sensing application.

6. Acknowledgment

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