Effect of CuO - Doping on Morphological and Electrical Properties of ZnO Thick Films

M. K. DEORE

Material Research Laboratory, Department of Physics,
M. V. P. Samaj's, Arts, Science and Commerce College, Ozar (Mig) 422206, India
E-mail: deoremadhav@rediffmail.com, deoremadhav63@gmail.com

Abstract

CuO - ZnO composite material was obtained by adding the Copper Chloride (CulCl2 . 2H2O) (Hexahydrate) powder of different weight percent (1 3, 5 7 and 9 wt %) and Analar Reagent grade (99.9 % pure) ZnO powder by mixing mechnochemically in acetone medium. The prepared materials were sintered at 1000^{o}C for 12h in air ambience and ball milled to ensure sufficiently fine particle size. The thick films of undoped ZnO and CuO 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 220 nm to 250 nm 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, CuO, Thick films, Screen printing, SEM, activation energy.

Introduction

ZnO is a II–VI group compound semiconductor with a hexagonal wurtzite crystal structure . It has a wide and direct band gap of 3.37 eV at 300 K and a large free exciton binding energy of 60 meV . It has unique physical and chemical properties, low-dimensional volume, high aspect ratio, light-matter interaction, cost-effectiveness and can be synthesized by various chemical and physical methods ZnO has become one of the most popular materials for electrical and optical applications over the time. It is promising material for many optoelectronic applications such as ultraviolet lasers, light-emitting diodes, p–n junction devices, thin-film transistor, solar cells, acoustic devices, chemical and biological sensors , areas like SAWdevices, varistors, transparent electrodes, gas sensors[1-15].

On the other hand, cupric oxide (CuO)is p-type semiconductors having band gap energy of 1.21 to 1.51 eV . CuO is an attractive material for photovoltaic applications since it has advantages of a relatively high absorption coefficient in the visible region, lowcost production, and is non-toxic. CuO has been established as a number of applications like in various fields such as dye sensitized solar cells , gas sensors, bio-sensors, nanofluid, photo detectors, energetic materials (EMs), field emissions, super capacitors, removal of inorganic pollutants, photo catalysis and magnetic storage media, gas sensors, solar photovoltaic, lithium ion electrode etc[16-27].

In order to obtain better crystallization quality and better optical and electrical properties, researchers have performed doping in metal oxides. Doping of the base martial was carried out by adding the additives in the base material. Zinc is an important transition metal element and $Zn2^{+}$ has close ionic

radius parameter to that of $Cu2^{+}$, which means that Zn can easily penetrate into CuO crystal lattice or substitute Cu position in the crystal [28,29].

In the present work the layer of ZnO has been fabricated in thick film form by screen printing technique. Thick film technology is often used to fabricate such sensors and possesses many advantages, for example, low cost, simple construction, small size and good sensing properties. In addition, this approach provides reproducible films consisting of well-defined microstructure with grain and grain boundaries that can be studied easily.

Experimental Procedure and Results

Preparation of composite materials

CuO - ZnO composite material were obtained by adding the Copper chloride ($CuCl_3$ •6H2O) (Hexahydrate) powder of different weight percent (0.5, 1 3, 5 and 7 wt %) with Analar Reagent grade (99.9 % pure) ZnO powder by mixing mechnochemically in acetone medium. The prepared materials were sintered at 1000^{o}C for 12h in air ambience and ball milled to ensure sufficiently fine particle size.

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) and organic solvents such as butyl cellulose, butyl carbitol acetate and terpineol, etc. This paste was screen-printed [30,31], on a glass substrate in a desired pattern (1.5cm X 0.5cm). The films were dried under infrared radiation for 45 minutes to remove the organic vehicle and then fired at a temperature of 550oC for 30 min, constant firing for 30 min at the peak temperature and then to attain the room temperature in a muffle furnace

Thickness measurements of the films

The range of thicknesses of the films was observed in the range from 65 to 75 mm. The reproducibility in thickness of the films was possible by maintaining the proper rheology and thixotropy of the paste.

Physical characterization CuO-doped ZnO films

Microstructural analysis of the films

It is known that gas sensing properties of metal oxide thick films are strongly dependent on its morphological features. A high surface area facilitates the chemisorption process by increasing the adsorption and desorption rates. 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).

Fig. 2 (a) shows the micrograph of undoped ZnO thick film. It consists of randomly distributed grains with smaller size and shape and with limited porosity. The grain size of films varies in between 220μ m to 250 μm.

Fig. 2 (b, c) shows that at lower concentration of dopant ,the numbers of CuO additives distributed on ZnO grains are very less as they are not sufficient to accelerate the sensing reaction with the target gas, hence it shows the poor sensitivity.

Fig. 2 (d) shows the micrograph of 5 and 7wt. % CuO -doped ZnO thick film which was most sensitive. It showed that the grain size decreases giving large effective surface area. The larger surface area gives more response to react with the target gas. The film seems to be highly porous for oxygen adsorption. Also CuO segregates at the grain boundaries. The segregation of CuO around the boundary of ZnO forms a hetro junction between ZnO(n) and CuO(p), facilitate the efficient charge transfer. Which enhance

sensitivity and selectivity under certain conditions.

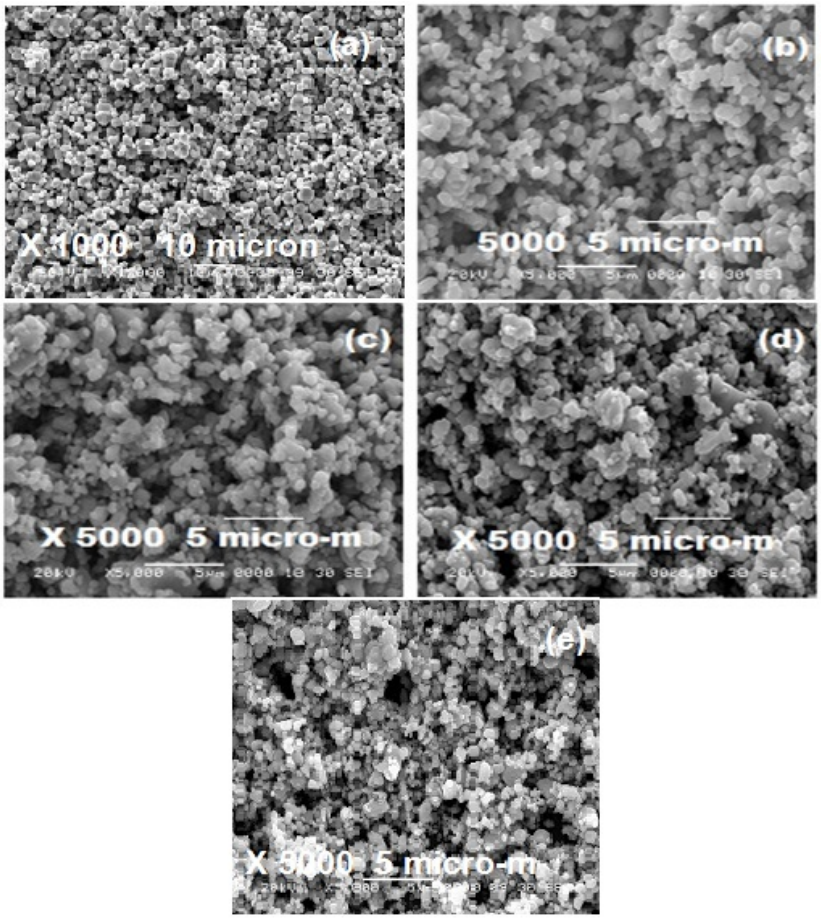

Figure 2: SEM images of (a) undoped –ZnO, (b) 1wt. % (c) 3wt. % (d) 5wt. % (e) 7 wt. % of CuO-doped ZnO films.

Fig. 2 (e), shows, large number of CuO additives which are distributed uniformly over ZnO. They are agglomerated around ZnO grains and the surface of the film becomes less porous. It resists reaching the target gas to the inter-grain boundary of CuO –ZnO. Also the agglomeration increases the particle size, hence effective surface to the volume ratio would decrease and less number of oxygen ions would be adsorbed on the film surface, hence it shows poor gas response.

Elemental analysis of the films

The Composition of undoped and CuO-doped ZnO thick films with different concentrations was analyzed by energy dispersive spectrometer.

Table 3 shows the composition of the film loaded at different level. The At. wt. % of Zn and O in each sample was observed to be non-stoichiometric. The ZnO film loaded with 5 wt. % CuO was observed to be most oxygen deficient. The deficiency or excess of the constituent material results in distorted band structure with corresponding increase in conductivity. The deficiency of the constituent material particles or an excess of it leads to the semi conducting behavior of the material [32,33].

Table 3: Quantative elemental analysis of CuO- ZnO films.

Sample	At. Wt. % of Elements			
	O	Zn	Cu	Total
ZnO (Undoped)	21.18	78.82	-	100
1 wt.% CuO-ZnO	41.46	58.27	0.27	100
3 wt.% CuO -ZnO	41.87	57.81	0.33	100
5 wt.% CuO -ZnO	39.91	59.92	0.17	100
7 wt.% CuO -ZnO	43.90	55.72	0.38	100

Electrical characterization undoped and CuO-doped ZnO films

Electrical conductivity of the films

The conductivity of CuO-doped ZnO thick films at constant temperature was calculated using the Eq. (4)[30].

$$\sigma = \frac{1}{(R \cdot b \cdot t)}\left(\frac{1}{\Omega - m}\right) \quad (4)$$

Where

σ = Conductivity of ZnO thick film at constant temp

t = thickness of the film sample ,

l = length of the thick film,

b = breadth of the thick film

Fig. 4 shows the variation in log (conductivity) with reciprocal of temperature of undoped and CuO-doped ZnO films. The increase in conductivity with increase in temperature could be attributed to negative temperature coefficient (NTC) of resistance and semi conducting nature of the film.

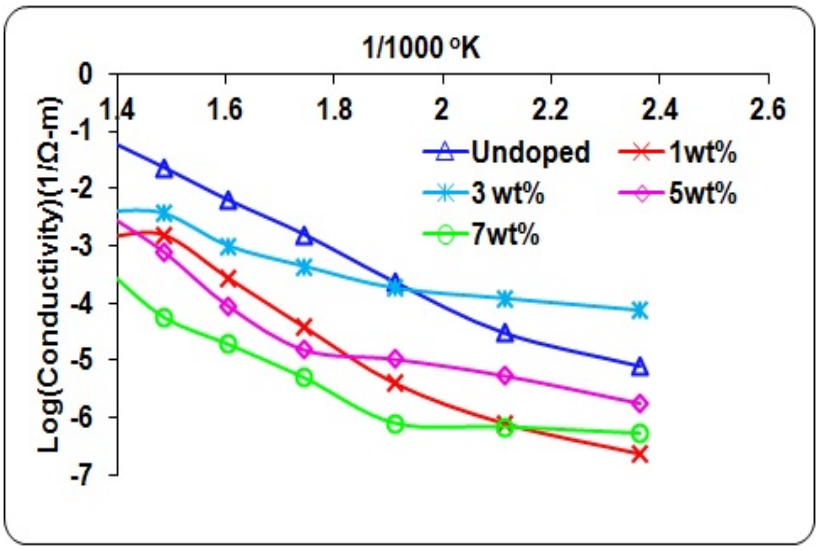

Figure 4: Conductivity- temperature profile of undoped and CuO-doped ZnO film.

The electrical conductivity of ZnO was decreased by doping Cu indicating the acceptor like behaviour of the Cu dopant. The four co-ordinated Zn^{2+}, Cu^{1+} and Cu^{2+} cations have ionic radii of 0.06, 0.06 and

0.057nm respectively[34], with stable electronic configuration, Zn^{2+} (3d10), Cu^{2+}(3d9) and Cu1(3d10). Diffusion at high firing temperature may lead defect reactions in which Cu^{2+} cations substitute Zn^{2+} cations in the wurtzite unit cell of ZnO. The stability of the coulomb forces of the interactions between the acceptor defect ($Cu^{1+}Zn$) and intrinsic ZnO donors (Zn_i or V_o) may occur by capture of an electron from the lattice.

West et al [34] proposed an interesting model of an associate donor-acceptor for CuZn where,

$$[Cu+Zn\ (3d10)] + Zn+i\ (5s1) \rightarrow \{ [Cu+Zn\ (3d10)] - Zn+i\ (4s1) \}^{10} \quad (5)$$

or Kroger and Vink notations,

$$Cu\bullet Zn + Zn\bullet i \rightarrow [\ CuZn - Zni\ ]^{\times} \quad (6)$$

According to the model, the creation of complex defects [CuZn - Zni]^x into ZnO/ZnO interface may contribute to increased barrier height. The presence of these types of defects compensates for n-type conductivity of ZnO, giving rise to n-type ZnO:Cu. Thus the conductivity decreases [36,35].

The decrease in film conductivity can be explained in terms of electron trapping by Cu 3d hole states of Cu^{2+}. The copper dopant after oxygen annealing in the ZnO films can be in the form of copper oxide. CuO (Cu^{2+}) has a Cu 3d9 4s0 O2p6 valence band configuration (neglecting hybridization) and may therefore trap electrons with the Cu 3d hole state. So conductivity is decreased,[36,35].

Activation energy of the films

Activation energy can be thought of as the height of the potential barrier or energy barrier separating two minima of potential energy. Activation energy of Al2O3 doped ZnO thick films were calculated from Arrhenius plot for different operating temperature regions by using Eq. (7).[37]

$$\sigma = \sigma_0 e^{-\Delta E / KT} \quad (7)$$

Where

σ = Conductance at constant temperature

ΔE = Activation energy of the electron transport in the conduction band,

K = Boltzmann constant and T = Absolute temperature

Activation energy can be thought of as the height of the potential barrier or energy barrier separating two minima of potential energy. Activation energy of CuO-doped ZnO thick films were calculated from Arrhenius plot for different operating temperature regions.

Table 4 shows variation in activation energy of undoped and CuO doped ZnO thick film resistor as a function of operating temperature.

Table 4: Activation energy of undoped and CuO-doped ZnO films.

Temperature (^oC)	Activation energy (ev)				
	Undoped	CuO- doped ZnO films			
	ZnO	1%	3%	5%	7%
100	0.02	0.205	0.036	0.210	0.144
150	0.027	0.244	0.041	0.233	0.174

200	0.039	0.258	0.039	0.247	0.194
250	0.032	0.260	0.036	0.265	0.214
300	0.071	0.243	0.023	0.285	0.201
350	0.109	0.224	0.007	0.275	0.191
400	0.151	0.203	0.023	0.249	0.182

Conclusions

From the results obtained, following conclusions can be made

i) It shows that the CuO –ZnO functional material can be obtained by mechanochemical method.
ii) The SEM analysis shows the surface morphology of the of undoped ZnO and CuO doped-ZnO thick films and it shows the films are porous in nature and petal-shaped grains oriented randomly of sizes varies from 220 nm to 250 nm were observed.
iii) 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.
iv) The electrical conductivity for CuO doped ZnO decrease as the dopant concentrations of CuO increase.
v) It also shows that the activation energy varies with the CuO dopant concentration. The film doped with 3 wt. % of CuO shows lowest activation energy than other doping concentrations. It may be due the barrier height decreases as CuO doping increases.
vi) CuO doped-ZnO thick films would be use full for gas sensing application.

References

[1] M. A. Mc Evoy and N. Correll. “Materials that couple sensing, actuation, computation and communication”. Science 347(6228), 2015.
[2] C. Klingshirn, “ZnO: Material, Physics and Applications” Chem PhysChem, 8(6): p. 782-803, 2007.
[3] D. R. Lide, “CRC Handbook of Chemistry and Physics”. 82 ed., LLC: CRC Press. 4-134, 2001/2.
[4] C. W. Bunn, “The lattice-dimensions of zinc oxide”. Proceedings of the Physical Society, 47(5): pp. 835-842, 1935.
[5] S. Ilican, M. Caglar, Y. Caglar, “Sn doping effects on the electro-optical properties of sol gel derived transparent ZnO films”.Appl. Surf. Sci., 256 (23), pp.7204-7210, 2010
[6] J. B. Lee, H. J. Lee, S. H. Seo, J. S. Park, “Characterization of undoped and Cu-doped ZnO films for surface acoustic wave applications”, Thin Solid Films 398–399,pp. 641-646, 2001.
[7] R. I. Lavrov, A. I. Ivon, I. M. Chernenko, “Comparative characteristics of silver and copper electrodes on ZnO varistor ceramics”, J. Eur. Ceram. Soc. (24),pp. 2591, 2004.
[8] Y. Ohya, H. Sakai, Y. Takahashi, “Preparation of transparent,electrically conducting ZnO film from zinc acetate and alkoxide”,J. Mat. Sci. (29),pp. 4099–4103, 1994.
[9] F. C. Lin, Y. Takao, Y. Shimizu, M. Egashira, “Hydrogen-sensing mechanism of zinc oxide varistor gas sensors”, Sens. Actuators B (25),pp. 843, 1999.
[10] A. Turner, G. Wilson, I. Kaube, Biosensors: Fundamentals and Applications. Oxford, UK: Oxford University Press. pp. 770, 1987.
[11] D. R. Clarke, Varistor Ceramics. J.Am.Ceram. Soc., 82(3): pp. 485-502, 1999..

[12] D. C Look, D. C. Reynolds, J. R. Sizelove, R. L. Jones, , "Electrical properties of bulk ZnO". Solid State Communications,105(6): pp. 399- 401, 1998.

[13] M .S. Wu, A. Azuma, T. Shiosaki, A. Kawabata, " Low-loss ZnO optical waveguides for SAW-AO applications", IEEE Trans. Ultrasonics Ferroelec.Freq. Control (36),pp. 442–445, 1989.

[14] M. K. Jayaraj, A. Antony, M. Ramachandran, "Transparent conducting zinc oxide thin film prepared by off-axis RF magnetron sputtering", Bull. Mater. Sci. (25),pp. 227–230, 2002.

[15] K. Keis, C. Bauer, G. Boschloo, A. Hagfeldt, K. Westermark, H. Rensmo, H. Siegbahn, "Nanostructured ZnO electrodes for dye-sensitized solar cell applications", J. Photochem. Photobiol. A: Chem. (148), pp. 57–64, 2002.

[16] R. N. Mariammal, K. Ramachandrana, G. Kalaiselvan, S. Arumugam, B. Renganathan, and D. Sastikumar, "Effect of magnetism on the ethanol sensitivity of undoped andMn-doped CuO nanoflakes". Appl. Surf. Sci., (270),pp. 545– 552, 2013.

[17] M. Hübner, C. E. Simion, Tomescu-St anoiu A., S. Pokhrel, N. Bârsan, .and U. Weimar, "Influence of humidity on CO sensing with p-type CuO thick film gas sensors". Sensor Actuat B, (153),pp. 347–353, 2011.

[18] Manish Kumar Verma, Vinay Gupta, "A highly sensitive SnO_2–CuO multilayered sensor structure for detection of H_2S gas". Sensor Actuat B, 166– 167, pp. 378– 385, 2012.

[19] S. Chandrasekaran, "A novel single step synthesis, high efficiency and cost effective photovoltaic applications of oxidized copper nano particles". Sol Energ Mat Sol C, (109), pp.220–2262013..

[20] J. Morales, L. Sanchez, F. Martın, J. R. Ramos-Barradob, and M. Sanchez, "Use of low-temperature nanostructured CuO thin films deposited by spray-pyrolysis in lithium cells". Thin Solid Films, (474), pp. 133– 140, 2005.

[21] K. Santra, C. K. Sarkar, M. K. Mukherjee, B. Ghosh, "Copper oxide thin films grown by plasma evaporation method", Thin Solid Films 213 (2), pp.226-229, 1992.

[22] D. M. Fernandes, R. Silva, A. A.W. Hechenleitner, .E Radovanovic, MAC Melo, "Synthesis and characterization of ZnO, CuO and a mixed Zn and Cu oxide", Materials Chemistry and Physics 115 (1), pp. 110-115,2009.

[23] M. Frietsch, F. Zudock, J. Goschnick and M. Bruns, "CuO catalatic membrane as selective trimmer for metal oxide gas sensor", Sensors Actuators B (65), pp. 379, 2002.

[24] M. Vaseem, A. Umar, Y. B. Hahn, D. H. Kim, K. S. Lee, J. S. Jang, J. S. Lee, "Flower-shaped CuO nanostructures: Structural, photocatalytic and XANES studies",Catalysis Communications 10 (1), pp.11-16,2008.

[25] S.B.B. Wang, C.H.H.Hsiao, S J J Chang, K.T.T.Lam, K. H. H. Wen, S. C. C. Hung, "A CuO nanowire infrared photo detector. Sensor" Actuat A: Phys, (171), pp. 207–11, 2011.

[26] J. Liu , J. Jin , Z. Deng, S. Z. Huang, Z. Y.Hu , L. Wang, "Tailoring CuO nanostructures for enhanced photo catalytic property". J Colloid Interface Sci., (384), pp.1–9, 2012.

[27] S. C. Ray, "Preparation of copper oxide thin film by the sol– gel-like dip technique and study of their structural and optical properties", Solar Energy Materials & Solar Cells 68\3-4, pp. 307-312, 2001.

[28] Ahmed M. Nawar1,, Nadia Abdel Aal, Nariman Said, Farid El-Tantawy, F. Yakuphanoglu, "Improving the optical and electrical properties of Zinc Oxide thin film by Cupric Oxide dopant, IOSR Journal of" Applied Physics (IOSR-JAP) ,Volume 6, Issue 4 Ver. II,pp. 17-22, Jul-Aug. 2014.

[29] Bikramkeshari Das, Tanushree Das, Kajal Parashar, S.K.S.Parashar, "Synthesis, Structural and Electrical Properties of Cu doped ZnO nanoparticles", Applied Science and Advanced Materials International Vol. 1 (1), pp. 16-20, September 2014.

[30] M. K. Deore, "Physical, Electrical Properties and Gas Sensing Performance of Pure and NiO-Modified ZnO Thick Films" Sensor Letters, Volume 11, Number 10, pp. 1919-1924, October 2013.

[31] G. H. Jain, V. B. Gaikwad, D. D. Kajale, R. M. Chaudhari,R. L. Patil,N. K.Pawar, M.K. Deore and L. A. Patil, "Gas Sensing Performance of pure and modified Barium Strontium Titanate Thick Film Resistors", Sensors and Transducers, (90),pp.160-173, (2008).

[32] L. A. Patil, D. R. Patil, "Heterocontact type CuO-modified SnO_2 sensor for the detection of a ppm level H_2S gas at room temperature", Sensors and Actuators B: Chemical 120 (1), 316-323,2006.

[33] L. A. Patil, G. H. Jain, "CuO-doped BSST thick film resistors for ppb level H_2S gas sensing at room temperature", *Sens. Actuat. B: Chem.* Vol.(123) pp. 246-253, 2007.

[34] C. West, D.J. Robbins, P.J. Dean, W. Hays, "The luminescence of copper in zinc oxide", Physica B & C (116),pp. 492–499, 1983.

[35] L. Chowa, O. Lupana, G. Chai, H. Khallaf, L.K. Ono, B. Roldan Cuenya I.M. Tiginyanuf, V.V. Ursakif, V. Sonte, A. Schulte, "Synthesis and characterization of Cu-doped ZnO one-dimensional structures for miniaturized sensor applications with faster response", Sensors and Actuators A (189),pp. 399–408, 2013..

[36] J. V. Bellini, M.R. Morelli, R.H.G.A. Kiminami, "Electrical properties of polycrystalline ZnO : Cu obtained from freeze-dried ZnO+copper(II) acetate powders", Journal of Materials science: Materials in Electronics (13),pp. 485, 2002.

[37] M. K. Deore, "Studies on Physical and Electrical Characterization of Al_2O_3-ZnO Composite Material and its Thick Films", International Journal of Science and Research (IJSR), Volume 4 Issue (11), pp.2240-2245, November, 2015.