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

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Abstract

CuO - ZnO composite material was obtained by adding the Copper Chloride (CuCl2 . 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 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 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 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 SAW devices, 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 Cu$^{2+}$, 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$_3$ &cdot6H$_2$O) (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 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.

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 550°C 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 hetero 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].
elemental analysis of CuO-ZnO films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>At. Wt. % of Elements</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>O</td>
</tr>
<tr>
<td>ZnO (Undoped)</td>
<td>21.18</td>
</tr>
<tr>
<td>1 wt.% CuO-ZnO</td>
<td>41.46</td>
</tr>
<tr>
<td>3 wt.% CuO-ZnO</td>
<td>41.87</td>
</tr>
<tr>
<td>5 wt.% CuO-ZnO</td>
<td>39.91</td>
</tr>
<tr>
<td>7 wt.% CuO-ZnO</td>
<td>43.90</td>
</tr>
</tbody>
</table>

Table 3: Quantative

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].

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

Where

- $\sigma$ = 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.

The electrical conductivity of ZnO was decreased by doping Cu indicating the acceptor like behaviour of the Cu dopant. The four co-ordinated $\text{Zn}^{2+}$, $\text{Cu}^{1+}$ and $\text{Cu}^{2+}$ 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 Cu\(^{1+}\) (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\(^{2+}\)) 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,

\[
[Cu+Zn (3d10)] + Zn+i (5s1) \rightarrow [Cu+Zn (3d10)] - Zn+i (4s1) \quad (5)
\]

or Kroger and Vink notations,

\[
Cu\cdot Zn + Zn\cdot i \rightarrow [CuZn - Zn\cdot i] \quad (6)
\]

According to the model, the creation of complex defects [CuZn - Zn\(_i\)]\(^+\) 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]

\[
s = s_0 e^{-\Delta E/kT} \quad (7)
\]

Where

\(s\) = Conductance at constant temperature
\(\Delta E\) = 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>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Activation energy (ev)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Undoped</td>
</tr>
<tr>
<td>ZnO</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>0.02</td>
</tr>
<tr>
<td>150</td>
<td>0.027</td>
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</table>
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 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 useful for gas sensing application.

References


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