Effect of Cu doping on LPG sensing properties of soft chemically grown nano-structured ZnO thin film

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Abstract. Zinc oxide (ZnO) thin film was grown by soft chemical route. Structural studies of ZnO thin film reveal hexagonal structure. The c/a ratio increase as the concentration of Cu (dopant) enhanced. Elemental analysis reveals the presence of Cu ions into ZnO matrix, which substitute at Zn site into the nano-structured ZnO crystal as it was presented in ball and stick model. Successful tailoring of band gap by doping was found in optical study and presented in band diagram model. The gas response was found to be 1.15 for 200ppm of gas concentration. The response and recovery times were found to be ~ 10 and 8 sec respectively.

1. Introduction
Amongst various II-VI compounds, ZnO is widely used metal oxide semiconductor for fabricating various types of gas sensors due to their versatile properties like wide energy band gap (3.3 eV), strong binding energy of 60 meV, higher transparency and low electron affinity. Due to these properties, ZnO is one of the promising material for many optoelectronic applications, such as ultraviolet lasers, light emitting diodes, transparent conductors, thin film transistor [1] etc. Doping is a widely used method for improving the opto-electrical properties of various semi conducting materials. Various materials like Al, Ga etc. on ZnO have been well studied for various types of applications. In general, the role of Cu as a luminescence activator and as a compensator of n-type materials is of considerable significance for II–VI compound semiconductor. Cu doped ZnO thin films has been used as phosphor and active material varistor. There are several reports available on the effect of Cu doping in ZnO and the variation in photoluminescent and magnetic properties. The effect of LPG sensing properties of spray deposited ZnO thin film at the operating temperature of 400 °C [2]. Mitra et al[3] have reduced the operating temperature upto 250°C after Pd doping. Further more, to reduce the operating temperature and to increase the response Cu was doped into the ZnO crystal. Generally, Cu doped ZnO is a widely used for CO sensor [4]. Cu doped ZnO thin-film is rarely used as liquid petroleum gas (LPG) sensor. With these motivations, in the present study we have doped Cu into ZnO thin film by SILAR technique for (LPG) sensor which enhances its importance for device grade application point of view. Also, we are introducing the energy band diagram to explain the role of Cu in the tailoring of band gap and a ball and stick model to represent how Cu doping controls the LPG sensing.

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2. Experimental details
The detailed description of the SILAR technique was mentioned in our earlier report [5]. In this paper we extend our results on physical modifications in ZnO thin films after Cu doping. For doping of Cu into the ZnO thin films, CuCl₂ was added into the solution at the rate of 2.5 % and 5 % respectively. Then the solution was stirred at constant speed at room temperature for about two hours for getting good quality thin films. The deposition was carried out by successive immersion and rinsing in the precursors and the double distilled water respectively for about 20 sec and 40 sec respectively. Cu doped ZnO thin films (~450 nm.) were annealed in air for about 2 hours.

The identifications of the crystal structure was carried out by CuKα (1.5405 Å) radiation using Burker D8 Discover in the scanning range of 200 to 600. The optical characterization of the films was done in the range 350–800 nm with the help of UV–Vis spectrophotometer lambda 25. The elemental analysis was done by EDAX an instrument which is in attachment with the SEM instrument. The x-ray photo electron spectroscopy study was performed in Indus 1, RRC CAT. The gas response was studied using an indigenous homemade gas sensor unit. The change in current before (air atmosphere) and after the insertion the test gas was measured using a digital picoammeter (model: DPM-111).

3. Result and discussion
Figure 1 shows the X-Ray diffraction (XRD) (Bruker D8 Discover) pattern of the pristine and Cu doped. The diffraction peaks observed at 2θ = 32.04º, 34.43º, 36.15º, 47.84º and 56.91º which attributes the (100), (002), (101), (102) and (110) planes for both (pristine and Cu doped) the cases respectively. Significantly, it is noted that the peak intensity increased with the increase in doping concentration. The peak (*) corresponds to the formation of copper oxide (JCPDS card no: 80-1917). As the doping concentration reaches 5% the CuO phase was found clearly. This attributes the thermal solubility limit of Cu in ZnO is below at lower concentration of Cu doping [6]. The comparative study of XRD pattern and the JCPDS card (75-0576) reveals the hexagonal structure (the pristine samples).

The calculated values of the lattice constant, bond length and the crystallite size calculated with the help of Sherrer formula, summarized in the table 1. The lattice constants a and c were calculated to be 3.25 Å and 5.20 Å, respectively refined by the least square method (c/a = 1.59) which is in well agreement with the reported value (c/a = 1.60). From table 1 it was found that as the doping concentration increased, the crystallite size increased while the anionic displacement decreased

Figure 2. shows the results of the optical absorption spectra for both the cases. From this figure the energy band gap (Eg) was found to be 3.22 eV for the pristine sample which is well matched with the values reported earlier [5]. But as the doping concentration increased, the Eg goes on decreasing. The reduction in band gap, with the increase in doping concentration, suggests that the Cu ions substitute

| Sample type | Lattice cons. a | Lattice cons. c | Crystallite size |
|-------------|----------------|----------------|-----------------|
| Pristine    | 3.2587         | 5.2016         | 10.35           |
| 2.5% Cu doped | 3.2312       | 5.1825         | 12.48           |
| 5% Cu doped | 3.2603         | 5.2636         | 14.65           |
Zn in the ZnO [6]. Inset of fig 2 shows the band diagram model for Cu doped ZnO film. The 3d state of Cu$^{2+}$ is located at 0.1 to 0.19 eV below the conduction band [7]. The acceptor level (Cu$^+$, h) is situated at about 0.45 eV above the valance band [7a] is formed after the excitation of Cu$^{2+}$ due to charge transfer. Zinc interstitial (Znoi) lie at 0.05 eV below the conduction band[8]. Considering these above mentioned facts, the change in band gap confirms the proper substitution of Cu in this case.

Furthermore, the compositional verification was studied by using EDAX and XPS analysis. Figure 3 a confirms the proper deposition of Cu in ZnO thin film. Other elements such as Si, Na etc. which are not (don’t mentioned here in the EDAX spectra) expected, may appear due to the glass substrate [9]. As the doping concentration enhanced, the peak position has shifted from the earlier reported peak positions. There was a shift in peak position was observed. These shifts in binding energy can be explained in terms of electronegativity ($\chi$)[10]. Figure 3.b shows the presence of a strong peak at BE 932.1, which signifies the peak of Cu 2p3/2 [11].

In case of Cu doped ZnO the valancy of Cu could be assumed to be +1 or +2 [12].The radius of Zn$^{2+}$, Cu$^{2+}$ and Cu$^+$ were found to be 0.74 nm, 0.72 nm and 0.96 nm respectively[13]. Considering the above mentioned facts we can conclude Cu$^{2+}$ might replace the Zn as shown in the ball and stick model (figure 3.c) of Cu doped ZnO crystal. This increase in crystallite size (confirms from the structural analysis) results in a lower density of grain boundaries which may behave as trap for free carriers and barrier for carrier transport which may attribute to the enhancement in conductivity [14]. So, in this case, the Cu may work like a bridge which may cause the improvement in gas response than the pristine sample.

Response is defined as the ratio of the current in gas atmosphere versus the current in air atmosphere. Figure 3 d shows the plot of response versus operating temperature of Cu doped ZnO thin film at 200 ppm of LPG gas concentration. This plot shows the increasing trend of gas response as a function of operating temperature. At 200°C it shows the best response then after it decreases. At first the Cu doped ZnO samples were kept into an airtight gas chamber and starts heating. As the temperature increases, the surface of the test sample absorbed the oxygen. Further more, as the temperature increases (≥ operating temperature) the oxygen molecule extract the electrons from the conduction band and the O$^2-$ converted into O$^2$. After attaining the operating temperature O$^2$ converted into O. The thermal energy of the gas molecule at lower temperature is insufficient to react with the O$^2-$ spices rendering the possibility of chemisorptions to be negligible [15].

The response and recovery time of a sensor can be defined as the time required for a film resistance to reach its 90% of its saturation value from the starting value of the gas exposure. Figure 6.b shows the response curve of the Cu doped ZnO thin film in the presence of 200 ppm of gas concentration. There was a sudden increase was found (upto 1.14). The response and recovery times for the Cu doped ZnO thin films were found to be 10 sec and 8 sec respectively.

**Figure 2.** Optical studies of pristine and Cu doped thin film

**Figure 3.** (a) EDAX and XPS spectra (c) Ball-stick model (d) gas sensing properties of Cu doped ZnO thin film
The inset of figure shows the comparative study of the gas response of ZnO and Cu doped thin film. This figure clearly depicts the enhancement in gas response after doping than the previously reported ZnO thin film[15].

4. Conclusion

Cu doped ZnO films with hexagonal phase were successfully deposited by SILAR technique at room temperature onto the glass substrates. The presence of CuO phase confirms the proper doping. The band diagram shows how the band gap was decreased from 3.22 eV to 3.13 eV with the increase in doping concentration which is well agreement with the previously reported values. The EDAX spectra and XPS study confirms the presence of Cu in the samples. The ball and stick model shows possible Cu substitution of into ZnO crystal. With these observations we can finally conclude that we have deposited the good quality Cu doped ZnO thin films at room temperature by cost effective chemical technique named SILAR.

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