Nanocrystalline pure and CuO doped ZnO thin films were prepared using spray pyrolysis technique. The zinc nitrate (0.1 M) and copper chloride (0.1 M) were used as starting precursor. These films were characterized by XRD, SEM and EDAX to observe structural, microstructural properties and elemental analysis respectively. It is observed that the average grain size was found to decrease from 190 to 90 nm, as the doping wt % of copper chloride in zinc nitrate solution goes on increasing. The sensing performances of pure and doped films were tested. The sensitivity goes on increasing with decreases in grain size (increase of copper chloride in zinc nitrate solution). The maximum sensitivity of $S = 35$ at $400 \, ^\circ C$ was found for films prepared from 10 wt % of copper chloride.

**Keywords:** GRAIN SIZE CONTROL, ZINC OXIDE, THIN FILMS, AMMONIA SENSOR, SPRAY PYROLYSIS.

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2. EXPERIMENTAL

2.1 Preparation of solution
Commercially available AR grade zinc nitrate and copper chloride were used as precursors to obtain pure and CuO doped ZnO thin films. The solution was prepared in deionized water. The reaction mixture was formed after adding the aqueous solutions in appropriate quantity after well steering.

2.2 Preparation of Pure ZnO thin film
Thin films of pure ZnO were prepared using following procedure. 0.1 M aqueous solution of \( \text{Zn(NO}_3\text{)}_2 \) was prepared in deionised water. The solution was allowed for spraying onto heated glass substrate at constant temperature of 350 °C. The sample was referred as S0.

2.3 Preparation of CuO doped ZnO thin films
Different wt % of CuO was doped into ZnO by adopting following procedure. The 0.1 M solutions of water soluble zinc nitrate and copper chloride prepared in deionised water. The stock solutions to be sprayed were prepared by mixing zinc nitrate and copper chloride in the proportion of : 99 : 1, 95 : 5 and 90 : 10. Each solution was filled in a spray gun and was allowed to spray onto heated glass substrate at constant temperature 350 °C. Zinc nitrate and copper chloride would be decomposes and pyrolyzed to obtain \( \text{Zn}_x\text{Cu}_{1-x} \) \( (x = 0.99, 0.95, 0.9) \). Thus the thin films with different wt % of CuO were obtained. The thin film samples were referred as S1, S2 and S3 respectively.

2.4 Anneling of pure and dopped thin films
The prepared pure and modified thin films were fired at 500 °C for 60 minute for complete oxidation.

2.5 Characterizations
The surface morphology of the thin films were studied using scanning electron microscope (JEOL JSM-6360 A). The quantitative elemental analysis of the thin film was carried out by computer controlled energy dispersive X-ray analyzer attached to the scanning electron microscope. The structural properties of the thin films were studied with X-ray diffractogram (Philips PW 1730) using Cu Kα radiation (\( \lambda = 1.5418 \) Å). The electrical and gas sensing characteristics were measured using a indigenous static gas sensing system.

3. RESULTS AND DISCUSSION

3.1 Structural analysis using XRD
The structure of the films was analyzed with X-ray diffractogram (RIGAKU DMAX 2500) using CuKα radiation with a wavelength 1.5418 Å.
Fig. 1 – X-ray diffractogram of samples: S0 (a), S1 (b), S2 (c), and S3 (d)
Fig. 1a through Fig. 1d are the X-ray diffractograms of pure ZnO, and CuO doped ZnO thin films (with CuCl$_2$ 1 ml, 5 ml, 10 ml) respectively. The observed peaks are matching well with ASTM reported data of pure ZnO. There are no prominent peaks of CuO associated in XRD pattern. It may be due to smaller wt % of CuO in comparison with ZnO. It reveals from XRD that the films are polycrystalline in nature. The average grain sizes as determined from Scherer formula and presented in Table 1. The d-values of as prepared films were compared with standard values and presented in Table 2.

**Table 1 – Dependence of grain size with CuCl$_2$ doping level**

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Solution in ml</th>
<th>Zn(NO$_3$)$_2$</th>
<th>CuCl$_2$</th>
<th>Total</th>
<th>Grain Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S0</td>
<td>100</td>
<td>100</td>
<td>0</td>
<td>100</td>
<td>190</td>
</tr>
<tr>
<td>S1</td>
<td>99</td>
<td>1</td>
<td>100</td>
<td>138</td>
<td></td>
</tr>
<tr>
<td>S2</td>
<td>95</td>
<td>5</td>
<td>100</td>
<td>110</td>
<td></td>
</tr>
<tr>
<td>S3</td>
<td>90</td>
<td>10</td>
<td>100</td>
<td>90</td>
<td></td>
</tr>
</tbody>
</table>

It is clear from Table 1 that, the average grain size was found to decrease from 190 to 90 nm, as the doping wt % of copper chloride in zinc nitrate solution goes on increasing.

**Table 2 – Comparison of observed and standard d values of pure and CuO doped ZnO thin films with different wt % of CuCl$_2$**

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Standard</th>
<th>Pure ZnO (d (Å))</th>
<th>CuO doped (1.27 %) (d (Å))</th>
<th>CuO doped (8.56 %) (d (Å))</th>
<th>CuO doped (9.66 %) (d (Å))</th>
<th>hkl</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.81</td>
<td>2.81</td>
<td>2.81</td>
<td>2.81</td>
<td>2.81</td>
<td>100</td>
</tr>
<tr>
<td>2</td>
<td>2.6</td>
<td>2.6</td>
<td>2.6</td>
<td>2.6</td>
<td>2.6</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>2.47</td>
<td>2.47</td>
<td>2.47</td>
<td>2.47</td>
<td>2.47</td>
<td>104</td>
</tr>
<tr>
<td>4</td>
<td>1.91</td>
<td>1.91</td>
<td>1.91</td>
<td>1.91</td>
<td>1.91</td>
<td>999</td>
</tr>
<tr>
<td>5</td>
<td>1.62</td>
<td>1.62</td>
<td>1.62</td>
<td>1.62</td>
<td>1.62</td>
<td>112</td>
</tr>
<tr>
<td>6</td>
<td>1.47</td>
<td>1.47</td>
<td>1.47</td>
<td>1.47</td>
<td>1.47</td>
<td>201</td>
</tr>
<tr>
<td>7</td>
<td>1.4</td>
<td>1.4</td>
<td>1.4</td>
<td>1.4</td>
<td>1.4</td>
<td>4</td>
</tr>
<tr>
<td>8</td>
<td>1.38</td>
<td>1.38</td>
<td>1.38</td>
<td>1.38</td>
<td>1.38</td>
<td>104</td>
</tr>
<tr>
<td>9</td>
<td>1.35</td>
<td>1.35</td>
<td>1.35</td>
<td>1.35</td>
<td>1.35</td>
<td>210</td>
</tr>
</tbody>
</table>

The d values of all the films were matched well with those in the PDF for ZnO.

**3.2 Elemental composition using EDAX**

The wt. % of Zn, Cu, O were obtained by EDAX technique are represented in Table 3. It is clear from the Table 3 that the thin films are zinc rich and oxygen deficient and hence are non stoichiometric in nature. With increase CuCl$_2$, the wt. % of Zn goes on decreasing. The thin film with 10 ml CuCl$_2$ doping was observed to be most oxygen deficient. The percentage of Zn is larger while percentage of Cu is smaller in sprayed S1, S2 and S3 samples.
Table 3 – The composition of CuO doped ZnO thin films

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Cu</th>
<th>O</th>
<th>CuO</th>
<th>Zn</th>
<th>O</th>
<th>ZnO</th>
</tr>
</thead>
<tbody>
<tr>
<td>S0</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>51.70</td>
<td>48.30</td>
<td>100</td>
</tr>
<tr>
<td>S1</td>
<td>0.66</td>
<td>0.61</td>
<td>1.27</td>
<td>51.42</td>
<td>47.31</td>
<td>98.73</td>
</tr>
<tr>
<td>S2</td>
<td>4.35</td>
<td>4.21</td>
<td>8.56</td>
<td>48.98</td>
<td>42.46</td>
<td>91.44</td>
</tr>
<tr>
<td>S3</td>
<td>5.18</td>
<td>4.48</td>
<td>9.66</td>
<td>48.48</td>
<td>41.86</td>
<td>90.34</td>
</tr>
</tbody>
</table>

3.3 Surface morphology using SEM

Fig. 2a depicts SEM image of pure and Fig. 2b through 2d represents SEM images of CuO doped ZnO thin films. Fig. 2a shows randomly distributed flat plate-like grains with shape distribution. Fig. 2b, 2c, 2d depicts the microstructure of a most sensitive CuO doped films (with CuCl₂ 1 ml, 5 ml, 10 ml) consisting of smaller spherical grains of Cu doped ZnO. The spherical grains may be due to large number of Cu – nucleation centers. The texture of sample S3 is seems to be relatively better than the pure ZnO sample S0. The sample S3 is expected to be more porous, giving larger effective area for the gas to react and in turn higher sensitivity may be expected. Image in Fig. 2b shows relatively larger spherical/elliptical shaped grains. Grain size is becoming more and more spherical, and numbers of grains are increasing with the increase of CuO percentage in the composition as evidenced from Fig. 2d. Atomic radius of Cu⁺² is smaller than Zn⁺². Larger the number of Cu⁺² ions, larger would be the nucleation centers. The feed would therefore, be divided and this would result into larger number of grains with smaller size and spherical shape.

![SEM images: S0 (a), S1 (b), S2 (c), and S3 (d).](image)
4. GAS SENSING CHARACTERISTICS

Gas response, selectivity, response time and recovery time are the important characteristics in gas sensing. Gas response is defined as the ratio of change in conductance of a sample on exposure to a test gas to the conductance in air. The gas response can be written as

$$S = \frac{G_a - G_g}{G_g} = \frac{\Delta G}{G_g}$$

Where $G_g$ and $G_a$ are the conductance in the presence of test gas and in air respectively. Selectivity can be defined as the ability of a sensor to respond to a certain gas in the presence of other gases. Response time is defined as the time needed for a sensor to attain 80% of maximum change in conductance upon the exposure to a test gas, while recovery time as the time taken by a sensor to get back 80% of the original conductance in air [11].

4.1 Sensitivity of pure and CuO doped ZnO films to NH$_3$ gas

Fig. 3 depicts the variation of gas response with operating temperature of CuO doped ZnO thin film for LPG, H$_2$, CO$_2$, C$_2$H$_5$OH, NH$_3$, Cl$_2$ gases. It is clear from figure that the nature of gas responses is similar for all gases. The response of NH$_3$ gas goes on increasing with operating temperature, reaches to maximum at 400°C and decreases with the further increase of operating temperature. CuO misfits would favour more oxygen ions to be adsorbed on the film surface. More the oxygen ions adsorbed, more electrons would be removed from the surface. This would make the film more resistive before exposure of NH$_3$ gas. On exposure of NH$_3$ gas, it would be oxidized and all the abstracted electrons would be returned back to material giving high conductivity. Smaller conductivity before exposure and larger conductivity after exposure of NH$_3$ gas would give higher gas response. The sensitivity of pure ZnO was observed to be smallest against the response of all the doped samples.

![Sensitivity of pure and CuO doped ZnO thin films to NH$_3$ as a function of temperature](image-url)
4.2 Selectivity for NH$_3$ against various gases at 400 °C

Fig. 4 depicts the selectivity of CuO doped sensor for NH$_3$ gas at 400 °C. It is clear from histogram that the sensitivity to NH$_3$ gas goes on increasing with the increase of CuO doping level in ZnO.

![Fig. 4 – Histogram comparing sensitivities of various gases at 400 °C](image)

5. DISCUSSION

The response to NH$_3$ gas would be attributed to adsorption – desorption mechanism. The ZnO is oxygen deficient. The excess zinc ions (due to oxygen vacancies) act as electron donors [13]. When reducing gas molecules like NH$_3$ reacts with negatively charged oxygen adsorbates, the trapped electrons are given back to conduction band of ZnO. The energy released during decomposition of adsorbed ammonia molecules would be sufficient for electrons to jump up into the conduction of zinc oxide, causing an increase in the conductivity of the sensor. An increase in operating temperature surely increases the thermal energy so as to stimulate the oxidation of NH3 given by possible reaction as,

$$2 \text{NH}_3 + 3 \text{O}_{\text{ZnO}} \rightarrow 3 \text{H}_2\text{O} + \text{N}_2 + 3 e^−$$

The reducing gas (NH$_3$) donates electrons to ZnO. Therefore the resistance decreases or the conductance increases. This is the reason why the gas response increases with operating temperature. The point at which the gas response reaches maximum is the actual thermal energy needed for the reaction to proceed. However the response decreases at higher operating temperatures, as the oxygen adsorbates are desorbed from the surface of the sensor [14]. In addition at high temperature the carrier concentration increases due to intrinsic thermal excitation and the Debye length decreases. This may be one of the reason for the decreased gas response at high temperature [15].

6. CONCLUSIONS

1) The pure and CuO doped ZnO thin films were successfully prepared by simple spray pyrolysis technique.
2) The average grain size was found to decrease from 190 to 90 nm, as the doping wt % of copper chloride in zinc nitrate solution goes on increasing.
3) Pure ZnO thin films are observed to be sensitive to NH$_3$ gas but showed poor sensitivity.
4) CuO doped ZnO sensors showed higher response to NH$_3$ gas as compare to pure ZnO.
5) The NH$_3$ response was goes on increasing with decrease in grain size.
6) Surface properties of the pure ZnO thin film could be conveniently customized (without affecting bulk properties) by doping technique.
7) The doping was observed to be an appropriate method to enhance sensitivity and selectivity to NH$_3$.

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