# Physical properties of semiconductor Cu: ZnO prepared by a simple route

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***Abstract:-***Physical properties of Zinc Oxide (ZnO) are studied with different doping in it. The dopants to study the varying physical properties of the ZnO semiconductor with respect to Copper (Cu), Aluminum (Al) and Gallium (Ga) semiconductor with changing doping by weight percent in it is studied in this paper. As discussed the physical properties included for the study are classified into three categories namely structural, electrical and the optical properties. The structural properties include X-ray Diffraction (XRD), Transmission Electron Microscopic Studies with the selected area electron diffraction patterns (TEM-ED) and Fourier Transform Infrared Spectroscopic studies (FTIR). The electrical properties include dc (direct component) electrical studies along with the gas sensing properties of the materials synthesized with the varying gases and its concentration. Its temperature effect by using given material as a thick film sensor is also studied. The gases used for the study are Ammonia ($NH_3$), Hydrogen disulphide ($H_2S$), Hydrogen ($H_2$) and Liquid Petroleum Gas (LPG). The different sensor by using the dopants shows remarkable sensing properties for different gases. Here in this section effect of Ga on the physical properties of ZnO is studied in detail.

***Keywords-*** ZnO, Hydrogen disulphide,sensors

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## 1. INTRODUCTION

Gas sensors have been widely used in the field of industry, agriculture, electronics and daily life. It plays a positive role in inspecting and monitoring harmful and inflammable gases. Semiconducting metal oxides are widely used as inexpensive and robust sensor material for toxic, hazardous and combustible gases and vapors in safety and automotive applications. Few semiconducting metal oxide materials used in these applications are ZnO, SnO2, In2O3, Fe2O3, NiO, etc [1-11]. Of which, zinc oxide (ZnO), an n-type semiconductor that displays a hexagonal crystalline wurtzite-type structure, with space group P63mc. The importance of ZnO is due to its unusual physical properties such as high conductance, chemical and thermal stability, wide and direct band gap of 3.37 eV and a high excitation binding energy of 60 MeV. Moreover, it is harmless to the environment [12-16]. Zinc oxide (ZnO) has emerged as one of the most promising materials due to its optical and electrical properties, high chemical and mechanical stability together with its abundance in nature. The effects of preparation conditions and/or doping on electrical property of ZnO-based thin films have been intensively studied because of their interesting functionalities such as transparent electric conductor, electroacoustic transducer, etc. [17,18]. Appropriate donor doping can produce the electronic defects that increase the influence of oxygen partial pressure on the conductivity. Nanto et al. showed that a lower operating temperature may be achieved by the doping effect, and a significant resistance change can be obtained in the doped ZnO rather than the undoped ZnO sensor, which results in a higher sensitivity [19].

Generally, nanometer-sized materials have been widely studied in recent years, due to their good gas sensitivity caused by high surface activity. Controlled ultra fine and narrow distribution of particle size of metal oxide powders can be obtained using various techniques, and the first step in keeping full control of the microstructure of the material is to control the preparation method of the starting powders. By selecting proper fabrication process, desired crystalline properties of metal oxides can be achieved.

## 2. EXPERIMENTAL DETAILS

### 2.1. Preparation of pure and doped ZnO nanocrystalline powders

All the chemicals used in this work are of AR grade (>99.9%). In a typical experiment of synthesis, appropriate quantity of zinc nitrate (Zn (NO3) 3·6H2O) was grounded for 30 min. in an agate mortar pestle and then dissolved in double distilled water. The aqueous solution was stirred for about 30 min. and subsequently transferred to Teflon lined stainless steel autoclave. The temperature of the autoclave was raised slowly to 180 0C and maintained for 10 h. Thereafter, the autoclave was allowed to cool naturally to room temperature and the resulting product washed several times with deionized water and absolute ethanol to remove the possible residue. Then the product was kept for drying at 100 0C in an oven for 12 h, which was followed by calcinations at 600 $^0$C for 6 h.

Depending on the required doping concentration, corresponding nitrate salt was added to the aqueous solution of zinc nitrate. In the present study, doping concentration of dopants was varied from 1.0 to 5.0-wt. %.

## 3. RESULTS AND DISCUSSION

### *3.1 Material characterization*

The XRD pattern of pure ZnO and Al3+-doped ZnO are provided in Fig. 1 (a-d). XRD patterns are indexed with ZnO with hexagonal structure. The XRD analysis confirms the formation of a solid solution between Al2O3 and ZnO within the concentration of doping investigated in this study. The lattice parameters of the prepared powder samples were calculated. Further, average grain size has been calculated with Debye-scherrer formula. The calculated values of lattice parameters and average grain size with respect to Al-dopands concentration are presented in Table 1. It can be seen that, there is a decrease in the lattice parameters of Al-doped samples as compared with pure ZnO, which may be due to lower ionic size of Al3+ than the host Zn2+.

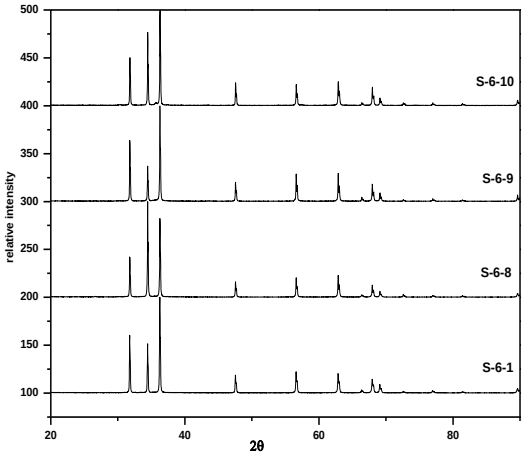


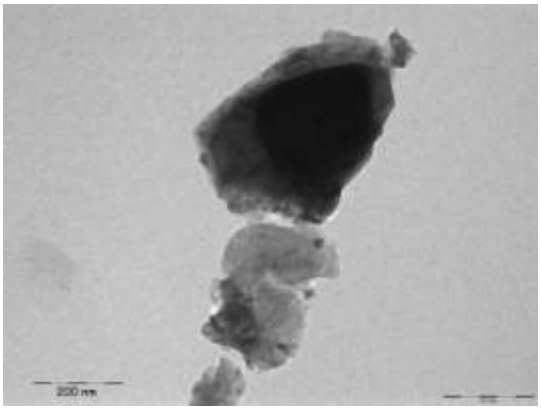

**Fig.1**. XRD patterns of (a) Pure ZnO, (b) ZnO: 1.0 wt.% $Ga_2O_3$, c)ZnO: 3.0 wt.% $Ga_2O_3$, and (d) ZnO: 5.0 wt.% $Ga_2O_3$ calcinated at 600 $^0$C.

| *$Ga_2O_3$ concentration (wt.%)* | *Lattice parameters (Å)* | Average grain size (nm) |
|---|---|---|
| 0 | a = b = 3.2499 (9) ; c = 5.2056 (2) | 78 |
| 1.0 | a = b = 3.2496 (2) ; c = 5.2060 (3) | 68 |
| 3.0 | a = b = 3.2497 (2) ; c = 5.2057 (4) | 64 |
| 5.0 | a = b = 3.2490 (2) ; c = 5.2053 (3) | 62 |

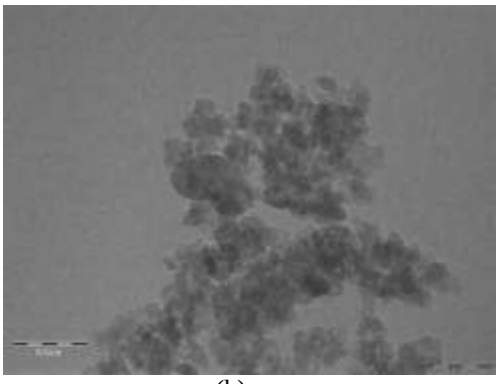
**Table 1:** Lattice parameters and average grain size of ZnO – Ga2O3 solid solution (5-7)

The average crystallite size calculated from XRD data agrres with the TEM results. The TEM images of pure and 3.0 wt.% Al3+-doped ZnO powders calcinated at 600 0C are provided in Fig. 2. The small amount of agglomerations can be observed in the TEM micrographs. In the same manner the TEM images with SAED of Cu and Ga doped ZnO are depicted in Fig. 3 (a-b)

The formation of ZnO wurtzite structure in the synthesized pure and doped ZnO powders was further supported by FT-IR spectra as shown in Fig. 4.The absorption peaks at about 3431 and 1590 cm-1 are attributed to the stretching vibration of the O-H bond and the bending vibration of H-O-H from water molecules, respectively. The absorption band at ~ 490 cm-1 is the stretching mode of ZnO [22-24].

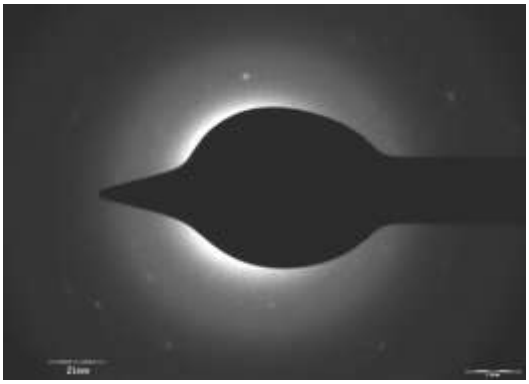


(a)



(b)

Fig.2. TEM photographs of (a) Pure ZnO and (b) 3.0 wt.% Al2O3 – doped ZnO calcinated at 600 0C.



(a)

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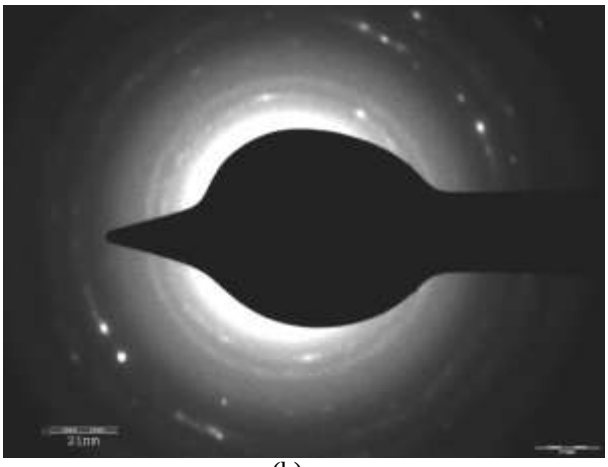


(b)

Fig. 3 (a-b) TEM images with SAED of Cu and Ga doped ZnO

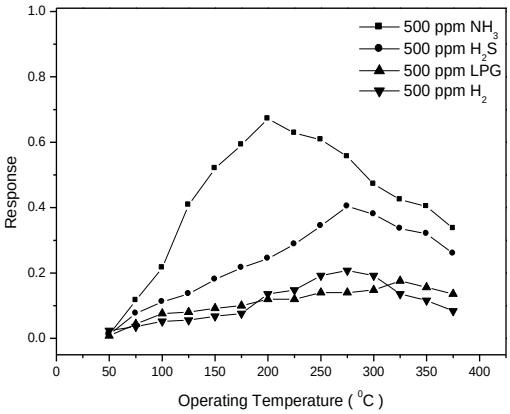



Fig. 4 The IR spectra of (a) Pure ZnO,
(b) ZnO: 1.0 wt.% Ga2O3, c) ZnO: 3.0 wt.% Ga2O3,
(d) ZnO: 5.0 wt.% Ga2O3 calcinated at 600 0C

### 3.3 Gas sensing behavior of Ga-doped ZnO

Fig. 5 shows the sensor response as a function of sensor operating temperature for doped and undoped elements for 500 ppm NH3 in air atmosphere. It is evident from these results that the sensor response of the undoped zinc oxide element is lesser compared to that of gallanium oxide doped in different concentrations. With 3.0 wt.% loading of Ga2O3, the element shows a maximum sensitivity to 500 ppm NH3 at an operating temperature of 150 0C. But at higher lanthanum oxide concentrations the sensitivity is decreased. The optimum concentration of Ga2O3 was found to be 3.0 wt.%.

It may be concluded that the modification of the zinc oxide surface with gallanium oxide is not only effective to improve the sensitivity but also retains the selectivity to NH3 and responded the sensor elements low concentrations as shown in Fig. 6(a-b)

Response and recovery times are the important parameter of gas sensor, which are defined as the time reached to 90% of the final signal. 3.0 wt.% Ga- doped ZnO sensors exhibit short response and recovery times. At 150°C, the times of 3.0 wt.% Ga-doped ZnO are 35 and 18 s, respectively.

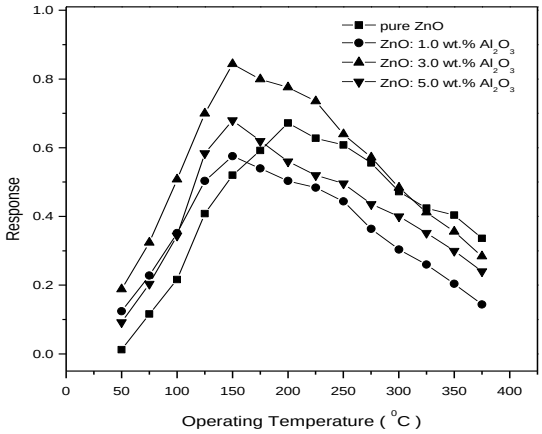
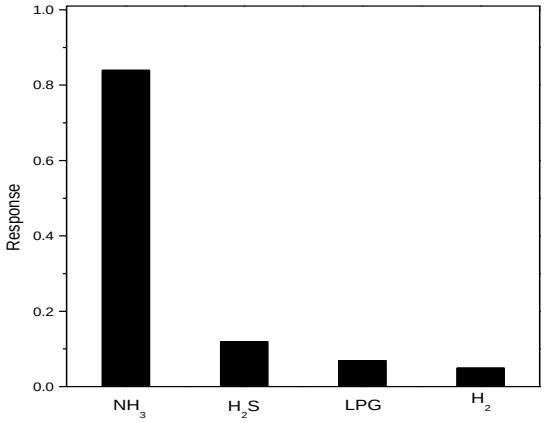
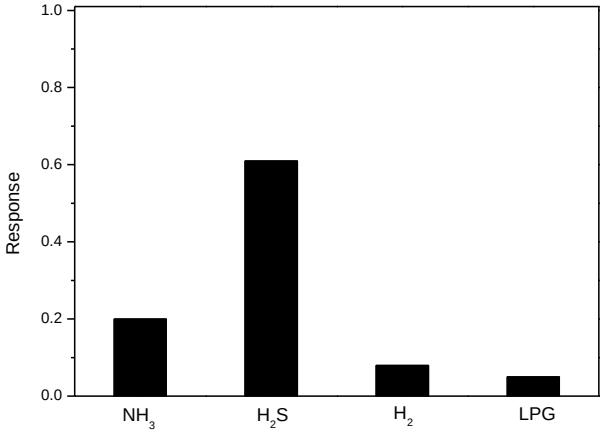



Fig.5. Sensor response of pure ZnO towards different reducing gases as a function of operating temperature.




(a)




(b)

Fig. 6: (a)Gas sensing response of Ga-doped ZnO to 500 ppm NH3(b)
(b) Sensor response to different gases

### \3.5 Gas sensing mechanism

The working principle of semiconductor gas sensors is based on the conductivity changes of the semiconductor materials because of its interaction with test gas molecules. When gas molecules are adsorbed on the surface of a semiconductor, electron transfer occurs between the semiconductor and the adsorbents. The sensing mechanism of ZnO gas sensors is usually based on the surface properties of the material [27, 28]. At elevated temperatures, adsorption of atmospheric oxygen takes place. The adsorbed oxygen extracts the conduction electrons from the surface region of ZnO grains, leaving positively charged donor ions behind. An electric field develops between the positively charged donor ions and the negatively charged oxygen ions such as O2-, O- or O2- on the surface [27, 29]. The more the oxygen ions are on the surface, the higher the potential barrier and therefore the higher the resistance [29]. As the concentration of target gas present in the ambient atmosphere increases, the amount of O2-, O- or O2- decreases due to the reaction with target gas molecules, resulting in a decrease in resistance. When temperature is varied with a given concentration of target gas, usually a peak appears in the sensor response versus operating temperature correlation.

## 4. CONCLUSION

In summary, nanocrystalline powders of pure and Al, Cu and Ga-doped ZnO were prepared successfully by a hydrothermal decomposition route. The as-prepared materials were tested for their respective response towards different reducing gases. The sensor made of the 3.0 wt.% Al3+-doped ZnO nanoparticles exhibits high response and good selectivity to NH3 as compared with pure ZnO nanoparticles. The sensor made of the 3.0 wt.% Cu2+-doped ZnO nanoparticles exhibits high response and good selectivity to H2S as compared with pure ZnO nanoparticles. Also the sensor realized the detection of NH3 with response time in seconds with excellent selectivity. Various gas-sensing responses to different gases may be because of the adsorption of the reducing gases and reaction between the gases and the adsorbed oxygen. All responses of the sensors were stable and repeatable.

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