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Physical properties of nanostructured Gallium (Ga) doped Zinc Oxide (ZnO) Semiconductor

Thakare NR*[1] , Bajpeyee AU[2] , Nande AV[3]

[1] Dept of Physics P R Pote (Patil) Engineering College Amravati (MS) India
[2] Dept of Physics Arts Science and Commerce College Kiran Nagar Amravati (MS) India
[3] Dept of Physics Gurunanak Science College Ballarpur (MS) India
Email: nilesh_thakarey@rediffmail.com

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ABSTRACT
Physical properties of Zinc Oxide (ZnO) are studied with different doping in it. The dopant to study the various properties of the ZnO semiconductor with respect to 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 different sensor by using the dopants shows remarkable sensing properties for different gases. The optical property includes UV-VIS measurements shows varying optical band gaps for the semiconductor materials to enable its semiconducting properties.

Keywords: ZnO, Gallium.

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, SnO_2, Fe_2O_3, NiO,In_2O_3 [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 (Zn0) 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 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]

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 (NO_3) 3 $\cdot 6H_2O$) 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 ^{0}C 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 ^{0}C 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. %. Samples with Ga_2O_3 concentration 1, 3, 5 wt. % are prepared.

X-RAY DIFFRACTION STUDIES

This section deals with the results and discussion of the samples in the form of powders which were prepared by using the simple hydrothermal chemical route. The powders formed were structurally characterized by using XRD technique. On the basis of XRD crystallite size is calculated by using Debay-Scherer formula [20]. The intensity peaks were matched and confirmed from the indexed peaks of the standard JCPDS data reported with the hexagonal wruitzit structure. The XRD patterns of Pure ZnO, 1.0 wt.% doped Ga2O3, 3.0 wt.% Ga2O3 and 5.0 wt.% Ga2O3 doped in ZnO and calcinated at fixed temperature 600^{o}C is shown in Figure [1]. The lattice parameters were calcualated from the XRD measurements. The effect of the Ga doping in the ZnO is also observed and studied. It is found that the lattice parameter decreases with the increase in doping concentration which are depicted along with crystallite size in Table [1]. The crystallite size is found to be decreased with the Ga addition in ZnO. Its TEM-ED studies of the material synthesised are also reported to supports XRD measurements. It also helps in the study of the sensing properties of the material in the form of thick film.

TRANSMISSION ELECTRON MICROSCOPY–ELECTRON DIFFRACTION PATTERN (TEM-ED)

Figure 3 shows at 600^{0}C, TEM-ED images of nano-crystalline gallium doped ZnO for 3 wt. % doping of Ga in ZnO. Size of nano-crystallites calculated from XRD data and particle size from TEM images are compared. It is observed that the crystallite size calculated from XRD has lower values than that of the particle size observed from the TEM-ED studies, but has good match. It may be due to the agglomerations of the crystallites to get diffused in the form of clusters

which can be seen from the images. The selected area corresponding electron-diffraction pattern is also shown for the hexagonal structure of 3 wt. % doping of Ga in ZnO. Some of the selected images are also shown in Figure. The particles within the range of 60 to 85 nm are observed. The average crystalline size calculated from XRD and particle size from the diffraction pattern is showing good match which means and supports nano structured material and its formation. At some miner positions diffused crystallite structure is seen but in an average all particles are spherical in nature supporting toward its gas enhanced sensing properties.

FOURIER TRANSFORM INFRARED SPECTROSCOPY (FT-IR)

The FTIR studies supports the chemical reaction occurred during the chemical process in the hydrothermal route. Figure 4 is FTIR spectra for the 0 wt %, 1 wt %, 3 wt % and 5 wt % Ga doped ZnO. It shows the transmission peaks at the selected peak positions indexed around 600 cm^{-1} as 1, 730 cm^{-1} as 2, 760 cm^{-1} as 3, 790 cm^{-1} as 4, 980 cm^{-1} as 5, 1100 cm^{-1} as 6, 1250 cm^{-1} as 7, 1500 cm^{-1} as 8, 1450 cm^{-1} as 9, 1760 cm^{-1} as 10 and 3740 cm^{-1} as 11 as shown. Peaks at these molecular vibrations correspond to that of doped and undoped ZnO. Especially the indexed positions of pure ZnO at 2, 5, 8 and 11 get inverted when compared with the doped samples. It may be due to the doping effect of Ga in ZnO. The molecular positions show its effect during the study of gas sensing properties of the doped and undoped ZnO which will be discussed separately. It is observed from the IR spectra that among the Curves b, c and d, b and d has approximately matched peaks but the curve c shows flatness at the indexed peak positions especially at positions 2, 3, 4, 5, 7, 8, 9, 10 and 11. It may be due to the change in its properties at 3 wt % doping in ZnO. Some peak assignments shows hydrogen bonded O-H stretch, which indicates presence of moister. The confirmation of the formation of the doped and undoped ZnO gets supported from these studies. [22-24]

Table 1: Lattice parameters and average grain size of ZnO – Ga_2O_3 solid solution [5-7]

Ga_2O_3 concen.(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

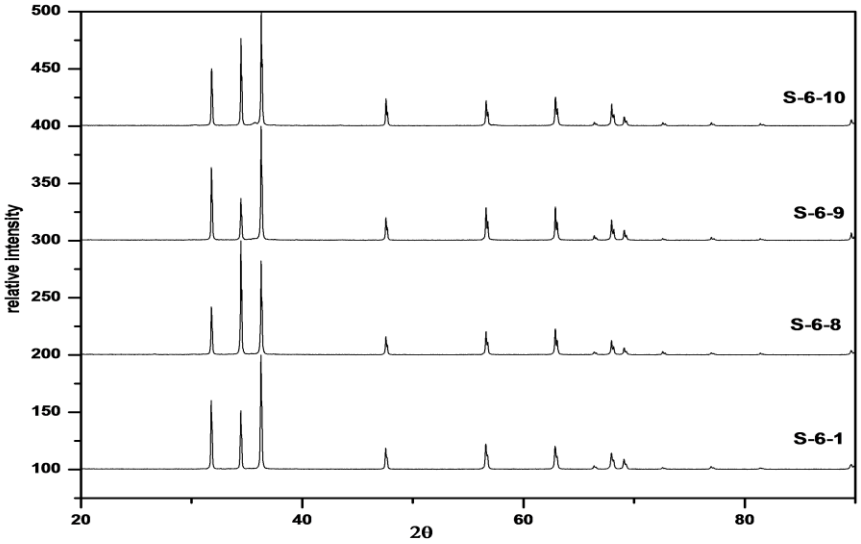
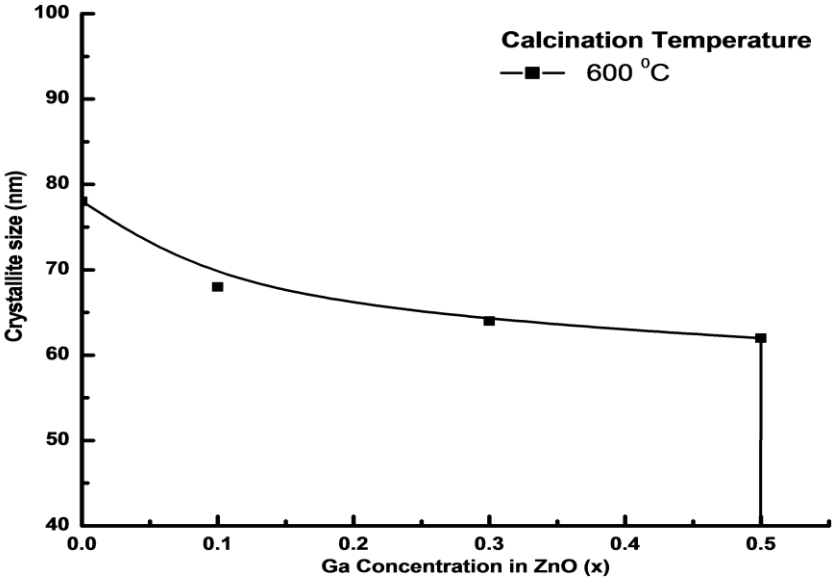


Fig.1. XRD patterns of (a) Pure ZnO, (b) ZnO: 1.0 wt.% Ga_2O_3, (c)ZnO: 3.0 wt.% Ga_2O_3, and(d) ZnO: 5.0 wt.% Ga_2O_3 calcinated at 600 ^{0}C.



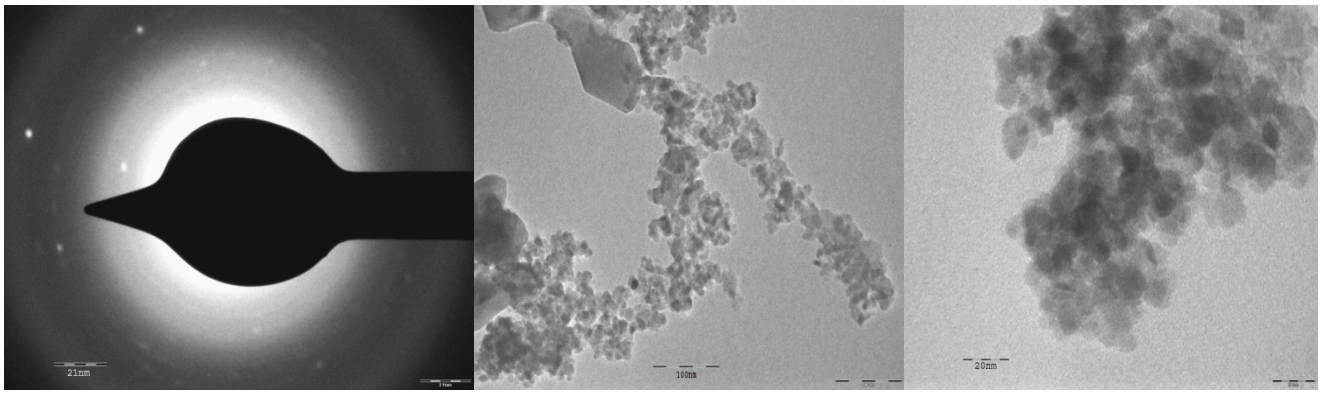


Fig.3. TEM image and Selected area electron diffraction patterns (ED) of 3.0 wt. % Ga_2O_3 – doped ZnO calcinated at 600 ^{0}C.

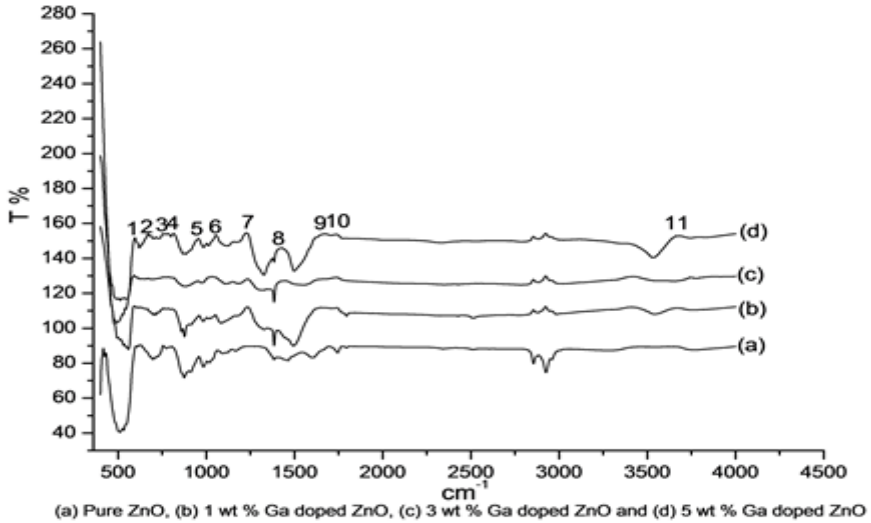


Fig. 4: The IR spectra of (a) Pure ZnO, (b) ZnO: 1.0 wt.% Ga_2O_3, c) ZnO: 3.0 wt.% Ga_2O_3, and (d) ZnO: 5.0 wt.% Ga_2O_3 calcinated at 600 ^{0}C.

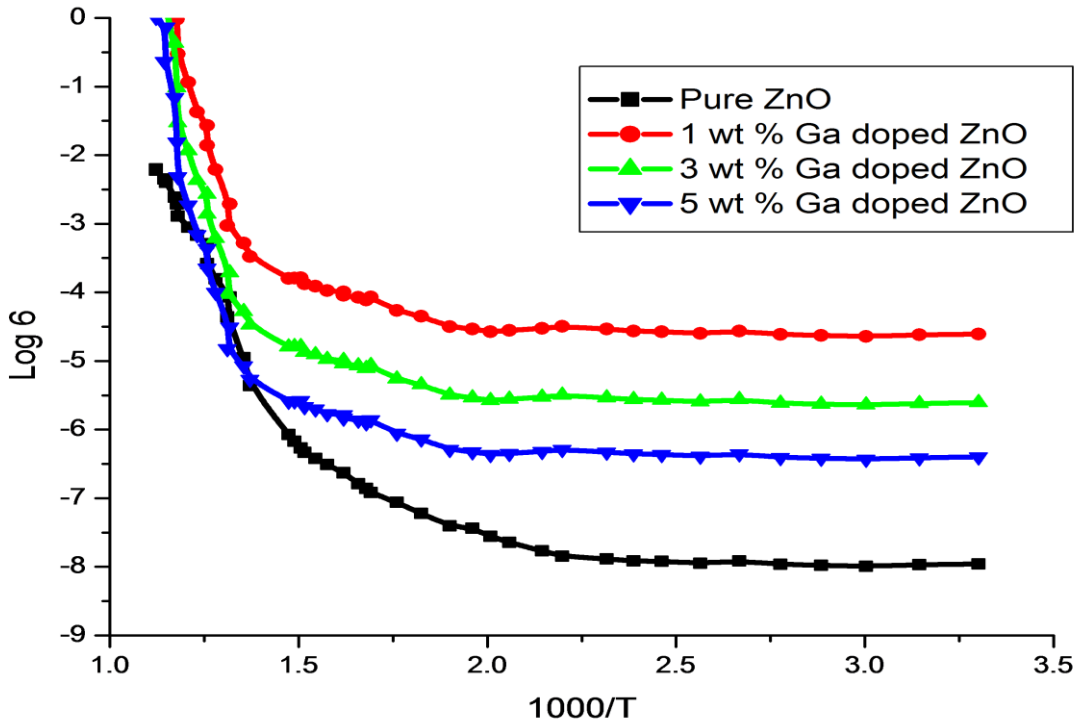
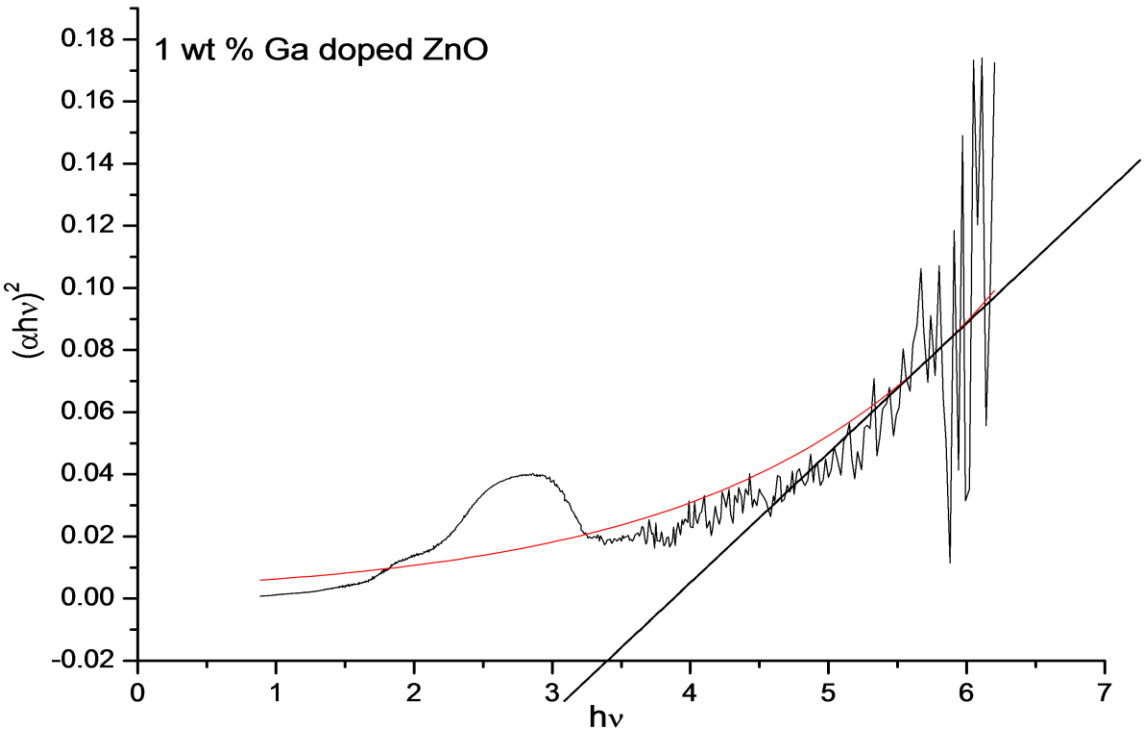
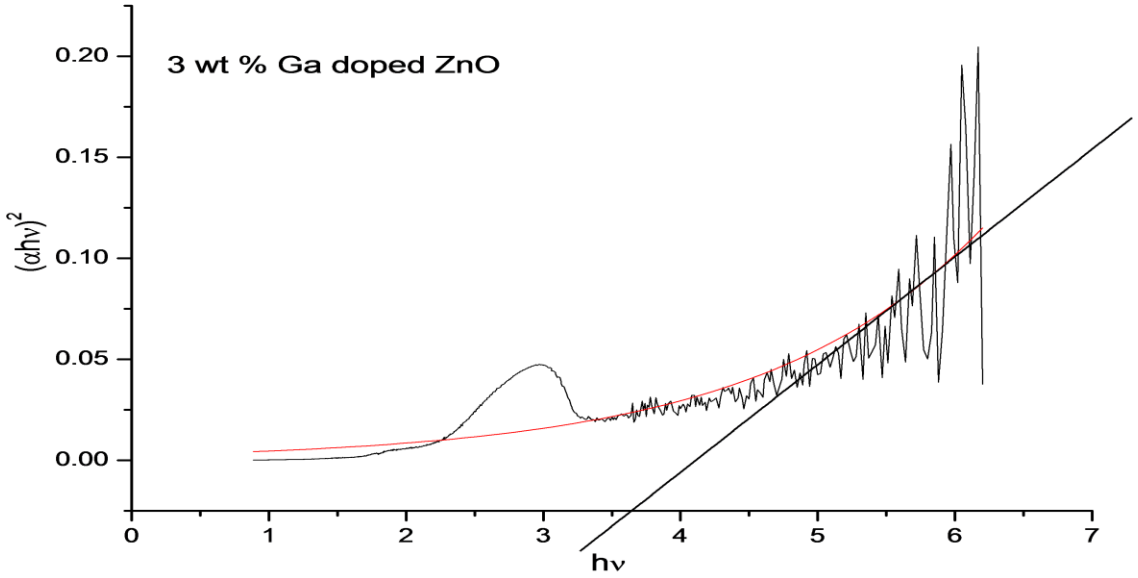
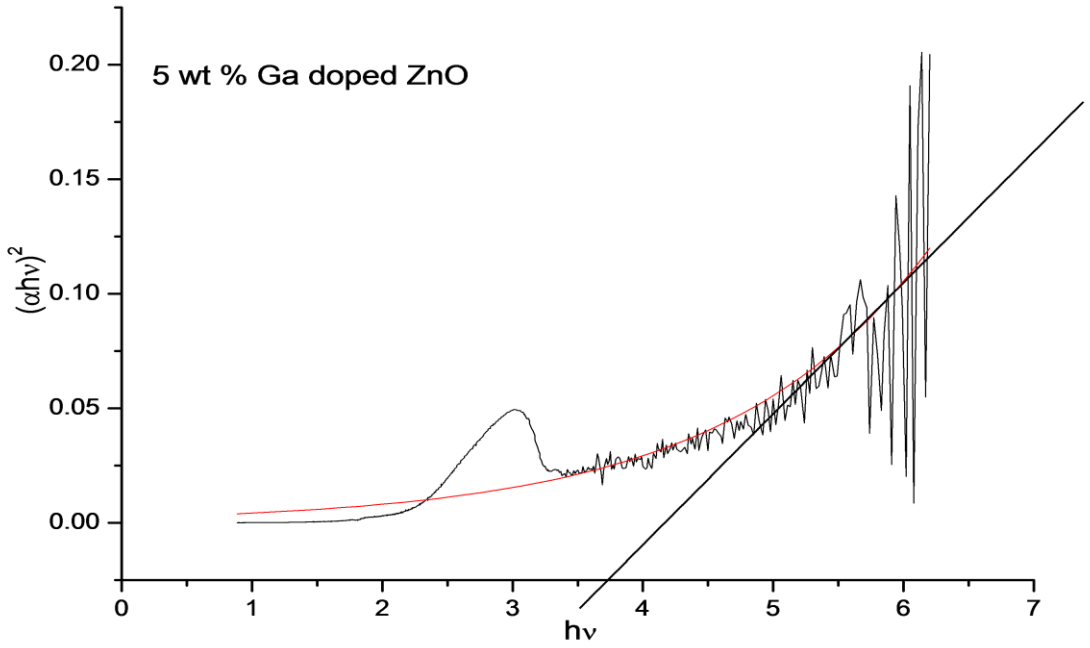


Fig 5: log σ vs. 1000/T plot for Ga doped ZnO







DC ELECTRICAL CONDUCTIVITY MEASUREMENTS

The calcined powders were pressed into circular pellet forms. Fig.5 shows log σ vs. 1000/T plot for Ga doped ZnO (x = 0, 0.1, 0.3 and 0.5) samples. It is seen that as the temperature increases conductivity also increases, it represents the semiconducting nature of the samples. In the beginning, the rate of increase of conductivity with temperature is small for all samples and then increases after a particular temperature, The rise in conductivity is observed around 571 K, 600 K, 650 K and 602 K for pure ZnO, 1 wt % Ga doped ZnO, 3 wt % Ga doped ZnO and 5 wt % Ga doped ZnO samples respectively. The transition temperature for doped samples is observed to be shifted to the higher temperature range as compared to the undoped. The

conductivity of 3 wt % Ga doped ZnO is greater than that of the others i.e 650 K. The direct activation energy is calculated from the slope of the log σ Vs 1000 / T plots in two sides of the curves for temperature regions. In low temperature region the values of activation energy are 0.0391 eV, 0.0366 eV, 0.0368 eV and 0.0367 eV and in high temperature region these are 0.4191 eV, 0.41 eV, 0.412 eV and 0.401 eV for pure ZnO, 1 wt % Ga doped ZnO, 3 wt % Ga doped ZnO and 5 wt % Ga doped ZnO samples respectively. The activation energies are varying with dopants. With slight change in it is for the sample with 3 wt % doping of Ga in ZnO is recoreded. Thus it is observed that in both the temperature regions, there is a slight change in activation energy due to the doping. But the activation energy values are found to be smaller in low temperature region as compared to the high temperature region. It supports the changing conduction mechanism of the samples with respect to temperature. The activation energy values indicate electronic conduction at lower temperatures and ionic conduction at higher temperatures. We are interested in electronic conduction of the semiconductor material for further study.

UV PROPERTIES OF GA DOPED ZNO

UV-Vis study as an optical property is one of the most important characteristics in connection to the study of the physical properties of the synthesized semiconducting material. It suggests the semiconducting behavior of the samples prepared and also its application and effects during the sensing of the different gases. The record of optical band gap for the all samples synthesized from UV-VIS measurements in the form of the graphical presentation is given here. Optical band gap is small for the pure sample (ZnO) with value 3.15 eV and increases for doped samples of which the respective values are 3.35 eV, 3.66 eV and 3.75 eV for the doped ZnO system with 1, 3 and 5 wt. % of Ga respectively.

CONCLUSION

1. 1.The physical properties which includes XRD, TEM, FTIR, dc conduction, gas sensing and UV-VIS study of 0, 1, 3 and 5 wt. % gallium doped ZnO system are reported here. The wruitzit hexagonal structure along with the crystallite size is confirmed from JCPDS data. The nano-crystallites are having spherical nature of the particles for all the samples. Further studied and responsible system with 3 wt % doped Ga in ZnO has average crystallite size of 64 nm.
2. It is found that the lattice parameter decreases with the increase in doping concentration which are depicted along with crystallite size. The decrease in a cell volume supports spherical nature of the particles which is discussed in the TEM-ED studies of the material synthesized. It also helps in the study of the sensing properties of the material in the form of thick film because of the increase in the surface area of the surface in contact with the given gases for a given volume.
   TEM-ED images of nano-crystalline gallium doped ZnO for 3 wt. % doping of Ga in ZnO are studied. Crystallite size calculated from XRD has lower values than that of the particle size observed from the TEM-ED studies. It may be due to the agglomerations of the crystallites to get diffused in the form of clusters. *The particles within the range of 60 to 85 nm are observed from TEM images.*
3. The FTIR studies supports the chemical reaction occurred during the chemical process in the hydrothermal route. From the peaks it can be concluded that molecular vibrations corresponds to doped and undoped ZnO. The molecular positions have normal effects of the doping shows its effect during the study of NH_3 gas sensing properties.
4. As the temperature increases, conductivity increases, which supports semiconducting nature of the samples. The rise in conductivity is observed around 650 ^oK for 3 wt % Ga doped ZnO shows higher transition temperature. Activation energy calculated has 0.0368 eV for lower and 0.412 eV for higher temperature range of 3 wt % Ga doped ZnO.
5. UV-VIS study as an optical property, It suggests the semiconducting behavior of the samples prepared and has value 3.66 eV for 3 wt. % of Ga doped ZnO

Conflicts of interest: The authors stated that no conflicts of interest.

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