Low-cost Fabrication of Cu doped ZnO (Zn$_{0.95}$Cu$_{0.05}$O) Film for Enhanced Gas Sensing Applications

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Abstract. Cu doped ZnO film (Zn$_{0.95}$Cu$_{0.05}$O) was fabricated by simple and cost-effective screen printing method. The structural and optical properties of prepared film was studied through X-ray diffraction (XRD) and UV-Vis spectroscopy techniques respectively. XRD analysis revealed the polycrystalline nature of prepared film with hexagonal structure. The optical band gap determined from UV-Vis analysis was found to be 3.40 eV. The gas sensing performance of prepared film was studied at room temperature toward different concentrations of NO$_2$ ranging in between 1ppm – 5ppm. The response and recovery time was noted as 13s and 92s respectively. All these outcomes shows that the Cu doped ZnO film shows enhanced gas sensing performance and can be utilized for industrial scale production of gas sensors.

1. Introduction
In the last some decades, semiconductor gas sensors dependent on the control of electrical conductivity upon the exposure to gases has pulled in extensive consideration attributable to their minimized size which encourage scaling down required in electronic circuits and basic detecting strategy [1, 2]. Consequently various materials have been created for gas detecting where the metal oxides that are truly and synthetically stable have been widely examined [3-5]. The electrical attributes of semiconducting metal oxide materials rely upon the structure of the encompassing gas climate. In view of this impact, the improvement of the gas sensors utilizing films of n-type zinc oxide is in progress [6-8]. However, this sort of gas sensor show an absence of selectivity because of a vague gas identification instrument and pretty much numerous kinds of diminishing gases are recognized. The improvement of particular sensors depends on the utilization of zinc oxide films doped with various guest ions as Cu, Al, Fe, Sn and so forth, and explicit interface between the particles to be distinguished and particles in the detecting materials [9-12]. Undoped ZnO films show n-type electrical conductivity and have inferior stability in humid condition or corrosion medium and properties are adjusted by adsorption of O$_2$, CO$_2$ and H$_2$O. Doping of the detecting zinc oxide films can deliver the deformities that expansion their effect on the sensors conductivity in gas encompassing and improve their properties with guest influences, for example, Cu, Al, Sn and so on. Various strategies have been employed to get undoped and doped films: magnetron sputtering [13], spray pyrolysis [14, 15], screen printing [16], sol–gel [17], and so forth. Among them, screen printing strategy has pulled in unique enthusiasm for setting up the zinc oxide films during the most recent
years because of its straightforwardness and minimal effort measures, capacity to accomplish large area deposition. The present work describes the low-cost fabrication of Cu doped ZnO film for NO \textsubscript{2} gas sensing applications.

2. Experimental
Cu doped ZnO (Zn\textsubscript{0.95}Cu\textsubscript{0.05}O) film were prepared by combination mixture of AR grade (99.9\% pure) zinc oxide (ZnO) and copper oxide (CuO) with non-hydrous ZnCl\textsubscript{2} as a bonding agent, following to the grinding with polyvinyl alcohol (PVA) as a binder. The resulting uniform paste was screen printed on ultrasonically cleaned silica glass substrate. The as-deposited Zn\textsubscript{0.95}Cu\textsubscript{0.05}O film was exposed to heat at 120\degree C for 1.5 h to partially eliminate the solvents and porous nature of film. The pre-heated film was then annealed at 500\degree C for 15min in programmable furnace at ambient condition for getting stable nature and decomposing of organic components. The annealed thin film was further used for structural, optical and gas sensing properties analysis. X-ray diffraction pattern was recorded on advanced Rigaku diffractometer in the 2\theta range of 20-80\degree using Cu-K\alpha radiation at room temperature. The optical studies were done by measuring transmittance spectra on Hitachi make UV-VIS spectrometer in the wavelength range of 350–800nm range. Gas sensing properties were studied using gas flow system [18].

3. Results and discussion
3.1. Structural analysis
To validate the film formation and crystal structure of Zn\textsubscript{0.95}Cu\textsubscript{0.05}O, the prepared film was examined using powder X-ray diffraction (XRD) technique. The diffraction pattern as well as FWHM curve of (101) plane as inset is shown in Figure 1. All the peak values matches well with that of hexagonal Wurtzite structure as per JCPDS card #36-1451 [19]. The inset of Figure 1 shows FWHM for the most intense (101) peak to calculate the crystallite size by using Debye-Scherer’s formula [20-22]. The estimated value of crystallite size was found to be 32nm.

![Fig. 1 X-ray diffraction pattern of Zn\textsubscript{0.95}Cu\textsubscript{0.05}O film](image)

3.2. Optical analysis
Figure 2 (a) shows the UV-visible transmittance spectrum of Zn\textsubscript{0.95}Cu\textsubscript{0.05}O film from which the band gap energy was calculated by using Tauc relation [23-25]. Figure 2 (b) shows the Tauc plot of $hv$ v/s $(\alpha hv)^2$ drawn for the optical band gap estimation [26-28]. The optical band gap of the film is obtained
by extrapolation of the linear portion of the graph between the $h\nu$ and $(\alpha h\nu)^2$. Using this the optical band was found to be order of $3.20\text{eV}$.

![Graph showing transmittance and Tauc plot for Zn$_{0.95}$Cu$_{0.05}$O film](image)

3.3. Gas sensing analysis
The gas sensitivity characteristics have been evaluated at room temperature for different gases such as NO$_2$, NH$_3$, H$_2$S, CH$_3$OH, Cl$_2$, C$_2$H$_5$OH etc at concentration of 5ppm. Fig. 3 (a) shows the selectivity plot for Zn$_{0.95}$Cu$_{0.05}$O film. It is observed from Fig. 3 (a) that, Zn$_{0.95}$Cu$_{0.05}$O film shows higher sensitivity towards NO$_2$ gas in comparison with the other gases. This shows that, Zn$_{0.95}$Cu$_{0.05}$O film is capable of sensing the NO$_2$ gas in a efficient way. Further the response and recovery characteristics of Zn$_{0.95}$Cu$_{0.05}$O film was recorded at room temperature for NO$_2$ gas concentration of 5ppm. Fig. 3 (b) shows the response-recovery plot for Zn$_{0.95}$Cu$_{0.05}$O film. It is noted from Fig. 3 (b) that, Zn$_{0.95}$Cu$_{0.05}$O film shows response and recovery time as 13s and 92s respectively. This shows that Zn$_{0.95}$Cu$_{0.05}$O film has a fast response time and higher sensitivity towards NO$_2$ gas sensing.

![Graph showing sensitivity and response-recovery plot for Zn$_{0.95}$Cu$_{0.05}$O film](image)

4. Conclusions
In conclusion, screen printing is a versatile and cost-effective technique to prepare the Cu doped ZnO film. The structural, optical and sensing studies indicate that such types of films are suitable for
sensing device and other electronic applications. XRD and optical studies revealed that prepared film have polycrystalline nature with hexagonal structure. From UV-study optical energy band gap transition has been confirmed and it is found to be 3.20eV. Thus, screen printing is cost-effective and simpler technique and can be used to fabricate polycrystalline semiconducting films having good stability and enhanced properties. The prepared film are suitable for NO₂ gas sensing devices as well as solar cells application.

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