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Abstract
Transparent Conducting Oxides (TCOs) are thin films of optically transparent and electrically conductive material. They are an important component in a number of electronic devices including liquid-crystal displays, OLEDs, touchscreens and photovoltaics etc. Indium tin oxide (ITO) is the most widely used TCO but its toxic effect and scarcity in nature causes for high cost of the product and hence technology needs a suitable replacement of it. Out of few replaceable materials, Aluminum doped Zinc Oxide (AZO) semiconductive material has been proven its potential replaceability due to its good transparency in the visible light as well as good conductivity. Also Zinc Oxide is abundant in nature and has no toxic effect. Pure ZnO and AZO sample were synthesized by simple low cost sol gel method and characterized optically and electrically. Effects of Al doping into ZnO nano crystal has been studied on transparency and conductivity aspects. It is observed that in both cases there is an optimum Al atoms concentration governed by the defects introduced by interstitial Al atoms in AZO nano crystal.

Keywords: TCO; AZO nanoparticles; Sol-Gel method; Transmission; Ion substitution effect.

1. Introduction
Today, nanoscience and nanotechnology are emerging as the operating as well as controlling of various fields of science and technology which are essential for in the present modern era. Nanoparticles are a part of nanomaterials that are defined as a single particles 1–100 nm in diameter. From last few years, nanoparticles have been a common material for the development of new cutting-edge applications in communications, energy storage, sensing, data storage, optics, transmission, environmental protection, cosmetics, biology, and medicine due to their important optical, electrical, and magnetic properties.

Indium tin oxide (ITO) is the most widely used TCO[1], but its toxic effect and scarcity in nature causes high cost of the product and hence technology needs a suitable replacement of it. Out of few replaceable materials, Aluminum doped Zinc Oxide (AZO) material has been proven its potential replaceability [2, 3] due to its close proximity to ITO. Also Zinc Oxide is abundant in nature and has no toxic effect. ZnO is a semiconductor which has direct band gap 3.4 eV [4]. In order to improve electrical and optical properties, ZnO film has been doped with many metal elements In, Ge, Al etc. We have doped aluminum in ZnO through a simple Sol-Gel technique [5].

Synthesis of Al-doped zinc oxide nano particle TCO material by simple Sol-Gel method
2. Experiment

2.1 Synthesis of Undoped ZnO and Al doped AZO nanoparticle.

We have synthesized undoped and Al-doped ZnO (AZO) nanoparticles through a simple and low cost Sol-Gel method. Undoped ZnO samples were prepared by dissolving 0.5 M of zinc acetate dihydrate $\text{Zn(CH}_3\text{COO)}_2 \cdot 2\text{H}_2\text{O}$ into 30 ml of ethanol. This solution was stirred at 80 °C for 1 hour. Then the solution allowed for crystallization by slowly annealing to room temperature. To prepare the AZO nanoparticles, different amounts of Aluminum acetate $\text{Al(OH)(CH}_3\text{COO)}_2$ were dissolved in a solution of zinc acetate dihydrate and polyethylene glycol as surfactant to gain concentration at 0% (AZO 0%), 2% (AZO 2%), 3% (AZO 3%) and 4% (AZO 4%) (g/mL), respectively. This precursor solution was sintered at 80°C for 1 hour with continuous stirring by magnetic stirrer. The solution slowly converted to gel. Then the gel was dried to powder at 60°C following by annealing process for crystallization. By this simple method, the nanoparticles have been successfully prepared.

2.2 Characterization.

The characterizations were conducted by X-Ray Diffraction (XRD), UV-visible spectroscopy and the crystallite size was calculated using the Scherrer’s formula:

$$D = \frac{K\lambda}{\beta \cos \theta}$$

where D is the average of crystallite size, $\beta$ is the full width at the half maximum of the diffraction peak, $\theta$ is the Bragg angle, $\lambda$ is the wavelength of X-ray used and $k$ is a constant. For transmission curve we used Beer’s law to extract transmission data from absorption data.

3. Results and Discussions

3.1 X-Ray Diffractions.

Crystal structures of the prepared undoped ZnO and Al doped AZO samples were examined by X-ray diffraction in the diffraction angle range 2$\theta$ = 10-80 °. X-Ray Diffraction [Fig. 1] shows the samples are polycrystalline nano-crystal

![XRD Patterns](image)

Figure 1. XRD patterns of Al doped ZnO at various Al concentrations.

X-ray photographs also shows that peak intensity is much higher for 3% Al doping sample than 4%. It indicates that crystal homogeneity breaking and more disorder phase appear for higher Al concentrations [6]. The crystallite size was calculated using the Scherrer’s formula. Calculated sizes of crystallites are given in the table 1.
Table 1: Calculation of crystal sizes of different Al doping concentrations

| Sample        | Peak position (2$\theta$) | FWHM (full width half maxima) | Crystal Size, D (nm) | Average Crystal size, $D_{av}$ (nm) |
|---------------|---------------------------|-------------------------------|----------------------|------------------------------------|
| 3% Al doped AZO | 11.74897                  | 0.32112                       | 24.86992009          | 26.99898166                        |
|               | 24.42357                  | 0.30341                       | 26.78952856          |                                    |
|               | 26.7863                   | 0.27836                       | 29.33749633          |                                    |
| 4% Al doped AZO | 11.44373                  | 0.28606                       | 27.91046939          | 30.011019                          |
|               | 21.43594                  | 0.33858                       | 23.88015154          |                                    |
|               | 26.50868                  | 0.21342                       | 38.24243873          |                                    |

So Al doping resulted in the increase in size of crystallites.

3.2 UV-Visible Optical Absorption.
Absorption spectra obtained in UV-visible spectroscopy shows that pure ZnO has absorption peak around 260nm [fig. 1] and Al doped samples have dual absorption peaks occur at two positions: one at around 275nm and other one at 300nm [fig. 2]. This indicates that there are two types of lattices: unaffected ZnO lattice peaked at 275nm and Al dope AZO lattices peaked at 325nm [7].

![Figure 1](image1.png)

**Figure 1.** UV-Vis optical absorption of ZnO.

![Figure 2](image2.png)

**Figure 2.** UV-Vis optical absorption of ZnO and AZO of different Al concentrations.

Optical band gap of samples has been determined with the help of Tauc relation:

\[(a\nu)^2 = A(\nu - E_g)\]  

(2)

where, $\alpha$ represents absorption coefficient, $A$ is a constant, $\nu$ is photon energy. Band gap value is found to be 3.6 eV for pure ZnO and 3.5 eV for AZO nanoparticles. It is also clear that band gap determined is higher than the value of bulk ZnO [8].


3.3 Transmission or Transparency of the materials.
Transmission data obtained from absorption data by using Beer’s law
\[
A = 2 \log_{10} \% T
\]
or
\[
T = 10^{(2-A)} \quad (3)
\]
has been plotted in fig. 3. It is clear from the graph that Undoped ZnO and Al-doped AZO samples below 4% Al concentration have transparency more than 80% and transparency reduces for higher Al concentrations. Reduction of transparencies may be due to scattering of photons by crystal defects created by doped aluminum atoms which took place in the interstitial positions or may be due to the impurity scattering present in the solution.

Figure 3. Transmission of AZO for different % of Al doping.

Figure 4. Current-Voltage characteristics of AZO Samples for different Al concentrations.

3.4 Study of Electrical properties.
For electrical and structural studies, DC electrical resistivity measurement has been done through a simple electrolysis method. Current-voltage characteristics of undoped and Al doped ZnO nanoparticles with five different doping concentrations (0%, 1%, 3%, 4%, 6%, 9%) are shown in Fig. 4. It is seen that the electrical current of the nanofluid increasing with Al dopant concentration upto 4% and then decreasing for higher Al concentrations [9]. For a clear picture of this variation, we have calculated resistivity using the equation
\[
\rho = R \times A / L \quad (4)
\]
where \(A\) is cross sectional area of the dipped electrodes within the solution, \(L\) is the separation of electrodes and \(R=V/I\), is the resistance plotted in fig. 5. Clearly, resistance decreases up to 4% Al concentrations and then decreases.

Figure 5. Variation of resistivity of AZO samples for different Al concentrations.
4. Discussion

All the above reported results show that Al doping into pure ZnO semiconductor crystal has prominent effect on crystallinity and transmission in visible range. Possible explanation of the existence of two peaks is as follows. Atomic radius of Al (125pm) is less than Zn atomic (139pm). Lattices where Zn substituted by Al atoms might shrink in volume. Atoms of shirked lattice become closure and there is a change in electrons distribution. This new distribution might introduce shallow energy states within the band gap causing reduction in excitation energy of the valance electrons. But all Zn ions couldn’t be replaced by dopant Al atoms. So, obviously there are two types of lattice exist within the AZO materials: pure ZnO lattice which has a peak at around 260-270nm and other one is Al substituted lattice which has a peak at a lower energy at 325nm.

Doped Al atoms have two sites to sit within ZnO crystal: lattice site by substituting of Zn$^{2+}$ ions and interstitial site of the crystal. Lattice site Al$^{3+}$ gives one free electron to the lattice and improves conductivity but interstitial site Al atoms do not give free electron rather distort the crystal and introduce defects in the crystal which in turn act as absorbing center of free electrons resulting decrease in conductivity. Initially when Al atoms concentration in solution is low, Al atoms try to occupy first lattice position replacing Zn atoms through chemical reaction prioritized by their electron affinity. So, conductivity increases. When Al concentration is high in solution, large percentage of Al atoms are accommodated in interstitial positions. Interstitial Al creates volume defect and acting as carrier trapping centers resulting reduction in conductivity of the sample. So for higher Al concentration, there is a competition between the effects of lattice Al and interstitial Al. Later effect dominates for higher Al concentrations.

5. Conclusions

Pure ZnO and Al doped ZnO (AZO) were synthesized by sol-gel method. The structural, optical and electrical properties of AZO nanoparticle have been investigated. Al doping has a prominent influence on the crystalline quality and structure of undoped ZnO. Two prominent peaks in absorption spectra of AZO samples indicate that ZnO and AZO lattice co-exist. Electrical characterization clearly established that a small fraction of Al atoms substitute lattice Zn- ions which provide free electrons resulting enhancement in conductivity but rest of Al atoms take accommodation in interstitial position which causes defects and act as trapping centers of charge carriers. This later effect reduces conductivity. So, conductivity of AZO sample is a competitive phenomenon. For better conductive samples, substitution effect has to be increased.

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