Synthesis, Electrochemical impedance analysis of silver-doped zinc oxide nanocrystallites

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Abstract— By using Co-Precipitation method, we have been prepared hexagonal structure of silver-doped Zinc Oxide (ZnO) nanocrystallites at room temperature. The structural characterization was carried out like Powder X-ray Diffraction (XRD). Scanning Electron Microscopy was used to study morphological analysis and EDX used to identify elements presented in prepared samples. Using the Scherrer formula, average size can be calculated. The XRD matched with JCPDS. The aim of the present work is to study the effect of electrochemical impedance frequency dependence properties of pure and silver-doped zinc oxide nanocrystallites were discussed in this paper.

Keywords — nanocrystallites, capping agents, co-precipitation, dislocation

1. INTRODUCTION

In Material Science and Technology, semiconductor nanostructures received great interest due to their exclusive size-dependent properties like energy gap scaling and the corresponding change in electrical, optical, mechanical properties [1]. ZnO material is an adaptable semiconductor [2], which has large bandgap $E_g = 3.37\text{eV}$ and high exciton binding energy 60 meV. In nanostructure family, zinc oxide is the richest one due to its unique property among all semiconducting materials [3]. ZnO is widely used in most applications such as solar cells, energy storage devices, optoelectronics, sensors, arrestors etc. Silver is a very good candidate as a acceptor to dope with ZnO [1]. In the present work, samples Undoped ZnO and Ag-doped ZnO are prepared using co-precipitation method at room temperature respectively, since this method is simple, easy and cost effective to obtain more ZnO nanoparticles. We reported structural, morphological and electrochemical studies of prepared samples which were beneficial for energy storage devices.

2. EXPERIMENTAL METHODS

A. Sample Preparation

Nanocrystalline powders of silver-doped Zinc oxide have been synthesized by the Co-Precipitation method using Zinc acetate and Sodium hydroxide as precursors. The capping agent used namely Glycerol to control the growth of the nanoparticle at room temperature. For silver doped zinc oxide, 0.001 M of Silver Nitrate (AgNO₃) solution added to the Zinc acetate solution. The precipitation was carried out over a reflux time of 600s for 100ml of reflux volume of each of the reacting solutions. The resulting white precipitated sample have been collected thoroughly were centrifuged and washed with de-ionized water repeatedly and then with methanol finally. The filtered sample was then dried in a hot air oven for 6-7h and grained to a fine powder with the help of mortar.
B. **Structural Characterization**

Powder X-ray diffraction studies were carried out using Cu-Kα radiation (λ = 1.5406 Å) (D8 Advance Bruker diffractometer) to determine the structural phase of the sample. The average size of the sample was determined from the line broadening of the X-ray diffraction peaks corrected for instrumental broadening using Scherer’s equation [4]. JCPDS software can be used to identify the h k l values and structure of the prepared samples.

C. **Electrochemical impedance spectroscopy**

The 6500B series of Precision Impedance Analyzer was used to take electrochemical impedance measurements for prepared samples at frequencies up to 120 MHz. To study the electrical properties the powdered sample was made it to pellet form of 2cm diameter and 16mm thickness using Motorized Hydraulic Press 10-Ton. The conductivity variation with frequencies, dielectric loss, Q-factor studies were analyzed for prepared samples.

3. **RESULTS AND DISCUSSIONS**

A. **X-ray diffraction study (XRD)**

The powder XRD patterns of the synthesized nanocrystalline using Glycerol samples are presented in Fig 1, 2. The five peaks observed at 20 values equal to 31.223, 33.507, 47.747, 56.102 and 69.309 for ZnO and 31.028, 33.492, 47.735, 57.003, 69.646 for Ag :ZnO prepared sample using Glycerol have been identified to be due to the planes with the indices (1 0 0), (0 0 2), (1 0 2), (1 1 0) and (2 0 1) respectively of the hexagonal structural phase of ZnO and Ag:ZnO (JCPDS No:89-0511,89-1397)[5]. From XRD patterns of prepared samples, it is very clear that the major reflections between 25° and 40° (20 values) indicates more crystalline regions and also the less intense peak at 47°,69° (20 values) indicate high crystalline of prepared samples.

![Fig.1: X-ray Diffractogram of ZnO](image-url)
B. Morphological analysis:

Scanning Electron Microscopy (SEM) study was used to determine the morphology of pure and Ag: ZnO nanocrystallites. Figure 2a and 2b represent the images of undoped ZnO and Ag: ZnO. According to the Figure (3) the morphology of undoped nanocrystallites is spherical having a diameter less than 20nm. The presence of some bigger particles might be attributed due to the aggregation of smaller particles. It is clear from the figure (3) that the smaller particles are aggregated each other. Also, the aggregation of the doped sample figure (4) is greater than the pure sample. The particle size changes considerably with respect to the incorporation of doping agent.

![Fig.3: SEM image of pure ZnO](image3.jpg)

![Fig.4: SEM image of Ag: ZnO](image4.jpg)
C. Elemental Analyses

The elemental analysis of undoped and Ag: ZnO samples were evaluated by Energy Dispersive X-Ray Analysis (EDX). Figure 5 and 6 illustrate the EDX analysis of undoped and Ag: ZnO nanocrystallites respectively. The atomic percentage of all the elements also represented within the figures. In the EDX spectra of undoped ZnO nanocrystallites, the presence of Zn and O elements have been identified, similarly for Ag: ZnO, the presence of Zn, O, Ag was exhibited.

![Fig.5: EDX image of pure ZnO](image)

![Fig.6: EDX image of Ag:ZnO](image)

D. Grain size Calculation

The average grain size was calculated using Scherrer equation (1) using the FWHM of all peaks. Most importantly, all of the XRD peaks were attributed to ZnO and no undesired peaks were observed [6] Scherrer equation is

\[
D = \frac{0.9 \lambda}{\beta \cos \theta} \quad (1)
\]

Where D is the grain size, \( \lambda \) is the wavelength of x-ray radiation, \( \beta \) is the full width at the half maximum (FWHM) of the ZnO and \( \theta \) is the diffraction angle. The FWHM is needed for calculation of grain size by Debye Scherrer equation. We have calculated FWHM with the help of XRDA software [7]. From Fig. 1a, 1b, we observed that the average crystallite size found to be 8 nm and 18 nm for ZnO and ZnO: Ag respectively. The radius of Ag\(^+\) ion is greater than that of Zn\(^{2+}\), so the average grain size increases when silver is added as a dopant. It concluded that average size of nanocrystallites not only depends on refluxing time but also depends on property of dopant added to the sample. Because of catalytic nature of dopant, the average size of undoped zinc oxide (ZnO) nanocrystallites smaller than silver doped zinc oxide (ZnO) nanocrystallites.
Smaller grain size maximizes the imperfect regions of the material, which is also supported by dislocation densities. This is due to volume imperfection occurs in a prepared sample. Table 1 show that volumes of the prepared crystallites are different by comparing XRD and JCPDS results.

**Table 1: volumes of the prepared crystallites**

| Sample | XRD | JCPDS |
|--------|-----|-------|
|        | Lattice parameter | Volume | Lattice parameter | Volume |
| ZnO    | a = 0.3051, c = 5.3445 | 50.562 2 | a = 3.249, c = 5.205 | 47.5800 |
| ZnO:Ag | a = 3.32, c = 5.42 | 51.72  | a = 3.253, c = 5.213 | 47.7734 |

*E. Dislocation Density*

The dislocation density $\sigma$ can be calculated by using formula (2).

Dislocation density $\sigma = 1/D^2$  \(\text{(2)}\)

Dislocation density is a measure of the number of dislocations in a unit volume of a crystalline material [8,12]. It is inversely proportional to the average size of a nanoparticle. Dislocation density describes dislocation of the lattice in a prepared sample. Table (2) represents dislocation density is inversely proportional to the average size of a sample.

From table 2, we concluded that average size of the nanocrystallites decreases to increases the dislocation density. It associated to the dislocation of the lattice. By decreasing average size of prepared nanocrystallites related to increasing dislocation of lattices in a sample.
Table 2: shows comparative results from XRD and JCPDS

| Sample    | Crystalline Size (nm) | $\sigma = \frac{1}{D^2}$ $10^{18}$ m$^{-2}$ |
|-----------|-----------------------|---------------------------------------------|
| ZnO       | 8                     | 0.0156                                      |
| ZnO:Ag    | 18                    | 0.0031                                      |

F. Electrochemical Analyses: Grain Effect

In Zinc oxide nanocrystallites, conductivity increases with frequency. Conductivity value reaches a maximum value of 0.275 mhos at frequency value is 7.5 MHz and the minimum value of 0.2 mhos at the frequency is 20 MHz. Two arcs represent grain interior effect and grain boundary effect respectively. The low-frequency arc represents grain interior effect and high-frequency region arc represents the grain boundary effect. Thus it is used in the confirmation of nanomaterial and also its one of the vital property.

G. Electrical Conductivity effect

Fig. 7, 8 shows the conductivity variation with frequency for zinc oxide and silver-doped zinc oxide respectively. It was found that the conductivity increases progressively with increasing frequency of the applied field. This was due to the electron hopping frequency.

At the low-frequency region, the conductivity does not change in the prepared sample. It was frequency independent behavior that characterizes the dc conductivity. At high-frequency value 10 MHz, electrical conductivity rapidly increases due to huge carrier hoping of material. The high-frequency region exhibits the behaviour of frequency dependence [9]. It is used to verify the semiconducting property of prepared material.

![Fig.7: Conductivity variation with frequency of ZnO](image-url)
Fig. 8: Ag: ZnO

**H. Q-factor**

Fig. 9 and 10 shows the variation of Q-factor (quality factor) with frequency for zinc oxide, silver doped zinc oxide respectively. It was clear that quality factor was high at low frequency region and low at high frequency region. It was found that higher Q-factor indicates a lower rate of energy loss relative to the stored energy of the resonator. The components such as inductors and capacitors are often quoted as having a certain Q factor or quality factor [10]. For oscillators high levels of Q result in improved stability and lower phase noise. This prepared material obeyed Q-factor property. The quality factor or Q factor is a measure of the performance of a capacitor and inductor in terms of its energy losses. It is one of the properties of energy storage material.

Fig. 9: Q-factor of pure ZnO

Fig. 10: Q-factor of pure Ag: ZnO
I. Dielectric Effect

Figure 11 and 12 represents the variation of dielectric constant at different frequencies for prepared undoped, silver doped zinc oxide nanocrystallites. It shows the variation of dielectric constant with respect to frequency characterized by space charge polarization [11].

The high dielectric constant value related to high ion jump orientation effect and increased space charge effect exhibited by the nanoparticles. Maximum numbers of atoms are present at the grain boundary region than the grain interior region. Due to this reason, the dielectric constant increased in the low-frequency region and decreased in the high-frequency region. Finally, the dielectric constant was attained at a constant level at very high frequencies. As a result, obtained, the prepared sample contains porosity and grain structures which are inhomogeneities in nature [12]. Polarization got decreased gradually as the frequency increases then it attained a constant value [13]. It is used to verify the electrical property of the prepared sample.

4. CONCLUSIONS

We observed that the average crystallite size found to be 8 nm and 18 nm for ZnO, ZnO:Ag, respectively. Average size variation depends on dopant added to the prepared sample. Smaller grain size maximizes the imperfect regions of the material, which is also supported by dislocation densities. This is due to volume imperfection occurs in a prepared sample. It was found that higher Q-factor indicates a lower rate of energy loss relative to the stored energy of the resonator. This prepared material obeyed Q-factor property. We concluded that prepared samples obeyed structural,
mechanical, electrical and catalytic properties. So it can be applicable in energy storage devices since Q factor value shows very less energy loss.

5. REFERENCES

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