Fabrication of ZnO and doped ZnO waveguides deposited by Spin Coating

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Abstract. In this paper, the synthesis of ZnO and doped Zn\footnotesize{1-x}Ag\footnotesize{x}O (where \(x=0.03\)) nanoparticles by co-precipitation is reported. The precursors used were Zinc Nitrate and Potassium hydroxide pellets. For doping, 3\% AgNO\footnotesize{3} in ZnNO\footnotesize{3} was considered as a separate buffer solution. The prepared nanoparticles were subsequently spin coated onto silica glass substrates at a constant chuck rate of 3000 rpm. The substrate acts as the lower cladding of a waveguide structure. The upper cladding is assumed to be air in the present investigation. The nanostructures of the ZnO powders in the doped and undoped cases were studied using X-ray Diffraction patterns. There was a decrease in the grain size with doping which increase the tunability of the powders to be used as photoluminescent devices. The optical characteristics of the sample were also investigated using UV-Visible spectrophotometer at 200-900 nm wavelengths. The photoluminescence peaks also report a dramatic increase in intensity at the same wavelength for the doped case compared to the undoped one.

1. Introduction
The use of nanocrystalline materials as potential candidates in the field of nano device fabrication has gained much attention in the recent past\cite{1-4}. Their unique electrical, optical and piezo electric properties have allowed extensive uses as semiconductor, acoustic wave and accousto-optical devices. Zinc oxide is a direct band gap (3.4 eV) II-VI compound and an n-type semiconductor which has a hexagonal wurtzite crystal structure with a number of alternating planes with tetrahedrally \(-\) coordinated Zn\footnotesize{2+} and O\footnotesize{2-} stacked alternately. Therefore it has attracted a lot of intense research for its unique properties and versatile applications in transparent electronics, UV light emitters, piezo electric devices, chemical sensors and spintronics\cite{5-8}.

The wide band gap of nano zinc oxide has been identified as a promising material for exhibiting the passage of various optical signals. Transition metal doped nanostructures enable intense optical effects such as variation of refractive index, grain size, adjustment of energy level surface states of Zn O leading to varied physical and optical properties\cite{9}. Nano zinc oxide is also non-toxic which offers it an additional edge to being increasingly user friendly.

The method of co-precipitation is an appropriate method for the synthesis of nanopowders especially because of the ease of preparation. It may be treated as a phenomenon whereby the fractional precipitation of a specified ion in a solution results in the precipitation of the target ion and also of other ions existing side by side in the solution. The excess precipitation of the other ions is an added advantage especially when dopants are present, though may be an impediment to the analytical process as well.

ZnO thin films depend critically on several physical and chemical parameters such as deposition technique, drying process, annealing temperature, pH of solution, concentration of solution etc. In the present work, we have fabricated ZnO and doped ZnO (Zn\footnotesize{1-x}Ag\footnotesize{x}O) thin films as a prerequisite for a waveguide structure. The nanoparticles were initially co precipitated, coated onto glass substrates by the sol gel process and characterized. The size and the thickness of the films were uniform and controlled.

2. Experimental
For the synthesis of ZnO nanoparticles, AR grade zinc nitrate dehydrate and potassium hydroxide pellets from MERCK laboratory were used without further purification. Polyvinylpyrrolidone (PVP) was used as a capping agent. In the present work, zinc oxide nanoparticles were prepared through chemical co-precipitation method in an aqueous medium at room temperature.

\[ \text{Zn}^{2+} + \text{OH}^{-} \rightarrow \text{Zn(OH)}_{2} \]

\[ \text{Zn(OH)}_{2} \rightarrow \text{Zn(OH)}_{2} \rightarrow \text{ZnO} + \text{H}_{2} \text{O} \]

\[ \text{ZnO} + \text{H}_{2} \text{O} \rightarrow \text{Zn(OH)}_{2} \]

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\[ \text{ZnO} + \text{H}_{2} \text{O} \rightarrow \text{Zn(OH)}_{2} \]
2.1 Co-precipitation of ZnO

The starting materials used for this study are AR grade zinc nitrate dihydrate $[\text{Zn(NO}_3)_2.2\text{H}_2\text{O}]$ , the zinc source and Potassium hydroxide pellets. In a typical synthesis of undoped ZnO, 0.1 M $\text{Zn(NO}_3)_2$ was dissolved in distilled water. 0.1 M of KOH was also simultaneously prepared by dissolving appropriate amounts of potassium hydroxide. The Zinc nitrate solution was magnetic stirred subsequently heating to a temperature of 50°C. The potassium hydroxide was added drop wise to produce a white, gelatinous zinc oxide complex. Meanwhile 0.05 g of PVP was also added so as to prevent agglomeration of the particles. The mixture was continuously stirred for two hours at room temperature, after addition of the KOH to a pH value of 8. The precipitates were filtered, centrifuged and dried at room temperature.

2.2 Co-precipitation of $\text{Zn}_{1-x}\text{Ag}_x\text{O}$

For the synthesis of ZnO doped with the transition metal silver, a separate buffer solution was made with 5% $\text{AgNO}_3$ in $\text{Zn(NO}_3)_2$ and dissolved in 50ml distilled water. It was then mixed with KOH following the same procedure as with undoped ZnO. The potassium hydroxide precipitates the silver oxide which appears as a grayish black complex.

2.3 Thin Films

ZnO thin films were prepared and deposited onto glass substrates in a colloidal consistency, the molarity was maintained for the undoped and the doped cases. The glass substrates were precleaned with detergent, and immersed overnight in sulfochromic solution. They were then washed with distilled water and rinsed with acetone and dried. The coating sol was dropped onto the glass substrates, the latter rotated at 3000 rpm for 20 s by using PHRL/TFA/002 Spin coater. After depositing by spin coating, film was dried at room temperature. The procedures from coating to drying were repeated ten times to obtain uniform thin undoped and doped ZnO films. The deposition time and the chuck rotation rate were found to be inversely proportional to the film thickness.

3. Results and discussion

3.1 X-Ray diffraction studies

The nanoparticles obtained were subjected to various analysis studies which gave insight into its various physical, chemical and thermal properties. For identifying the specimen’s crystalline phases and measuring its structural properties, homogenous and inhomogeneous the diffraction pattern was used. Consequently, the change in d-spacing, which is the result of the change of lattice constants under a strain [10] was measured. Peak broadening, independent of $\sin \theta$ caused by the finite size of crystallites was observed. Both crystallite sizes and the inhomogeneous strain contribute to the peak width, which may be separately determined by the careful analysis of peak shapes [11,12]. In the case of no inhomogeneous strain, the crystallite size, $D$, can be calculated from the peak width with the Scherer’s formula  

$$D = \frac{K \lambda}{B \cos \theta_B}$$

, where $\lambda$ is the X-ray wavelength, $B$ is the full width of height maximum of a diffraction peak, $\theta_B$ is the diffraction angle, and $K$ is the Scherer’s constant of the order of unity for usual crystal [12].
Figure 1.a. XRD pattern of undoped ZnO nanoparticles synthesized peaks observed are at $2\theta = 36.481, 34.640, 31.996, 37.24, 56.800, 63.042$ corresponding to the lattice planes (111), (111), (111), (220), (220) respectively (JCPDS card no: 77-0191)

Figure 1.b. XRD pattern of doped ZnO nanoparticles synthesized peaks observed are at $2\theta = 36.446, 34.596, 31.957, 37.24, 56.773, 63.008$ corresponding to the lattice planes (111), (111), (111), (220), (220) respectively (JCPDS card no: 77-0191)

The XRD pattern of undoped ZnO powders show diffraction peaks from various directions of ZnO, the powders being polycrystalline exhibit intense peaks at (111) and (220).

| Sample Name | Data observed from XRD | D (nm) | JCPDS data corresponding to observed from XRD pattern | Strain | Dislocation |
|-------------|------------------------|--------|--------------------------------------------------|--------|-------------|
| Undoped ZnO | 2th (degree)           | Phase  | Cubic phase | Hexagonal phase |       |             |
|             |                        |        | $2\theta$ hkl |                     |       |             |
| 36.481      | C                      | 23.495 | 36.326 | 111            | 8.87x10$^{-4}$ | 6.561x10$^{-4}$ |
| 31.996      | C                      | 25.428 | 36.326 | 111            | 9.890x10$^{-4}$ | 8.141x10$^{-4}$ |
| 56.800      | C                      | 20.385 | 61.199 | 220            | 1.111x10$^{-4}$ | 1.028x10$^{-4}$ |
| 63.042      | C                      | 17.921 | 61.199 | 220            | 9.240x10$^{-4}$ | 7.107x10$^{-4}$ |
Doped with AgNO$_3$

|                | 36.446 | C     | 20.599 | 36.326 | 111   | 1.682x10$^{-3}$ | 2.356x10$^{-3}$ |
|----------------|--------|-------|--------|--------|-------|----------------|----------------|
|                | 31.957 | C     | 21.976 | 36.326 | 111   | 1.577x10$^{-3}$ | 2.070x10$^{-3}$ |
|                | 56.773 | C     | 17.567 | 61.199 | 220   | 1.973x10$^{-3}$ | 3.240x10$^{-3}$ |
|                | 63.008 | C     | 16.549 | 61.199 | 220   | 2.094x10$^{-3}$ | 3.651x10$^{-3}$ |

Table 1. Tabulated XRD values from graph and from the JCPDS card no:77-0191 data. The strain and dislocation values for the corresponding (hkl) planes is also listed in the doped and undoped cases.

The prepared sample as observed, is in the cubic phase of ZnO nanoparticles. The average sizes for the particle was calculated from the Debye Scherer’s formula. The average size of the particle $D$ for the doped case was about 18 nm in whereas it is 25 nm in the undoped case. This accounts for the decrease in grain size and thereby increase in the band gap energy which gives more space for excitonic transitions. The crystallite size ($D$) and the corresponding strain ($\varepsilon$) and dislocation density ($\rho$) were estimated as tabulated for the doped and undoped variants.

### 3.2 Optical studies

The optical absorption spectra of ZnO and Zn$_{1-x}$ Ag$_x$O ($x=0.05$) by UV-viz spectrophotometer in the range 200 to 1000 nm were studied. The figure 2(a) depicts the excitonic absorption peak for both the doped and undoped samples is seen around 230 nm. Doping incorporates a fairly blue shift as can be seen from the curve 2(b) for the doped case. The peak is intense at a particular temperature and evidence suggests that the peaks become broader as the temperature increases $^{[13]}$.

![Figure 2](image-url) Absorption spectrum measured at various wavelengths under a spectral range of 105 to 3300 nm (UV-SHIMADZU 2401 PC) and plotted by a recorder between 100 to 1000 nm (a) undoped (b) doped Zn$_{1-x}$ Ag$_x$O

A UV-Visible spectrophotometer was used to measure the amount of light absorbed at each wavelength of the UV and visible regions of the electromagnetic spectrum. This gave information about electronic transitions in the sample. Absorption of radiation by a sample was measured at various wavelengths under a spectral range of 105 to 3300 nm (UV-SHIMADZU 2401 PC) and plotted by a recorder between 100 to 1000 nm to give the spectrum, a plot of the wavelength of the entire region versus the absorption of light at each wavelength. The samples were dispersed in water to record absorption spectra. The doped ZnO exhibits high transparency in the visible region as shown.
Figure 3. Photoluminescence spectra recorded at the visible range (400-700 nm). Sharp peaks are observed at 420 nm and 470 nm in (a) undoped (b) doped.

The photoluminescence spectra of undoped and doped ZnO shows two photoluminescent emission spectra at 420 and 470 nm respectively. The doped variant shows a slight blue shift in the emission spectra. The sharp peak corresponds to band to band transition. The less intense peaks if occur correspond to deep level defects, which are uncommon in the current investigation. The intensity peaks in the doped structure shows a dramatic increase at the two wavelength regions. The scope of the doped variant as a good photoluminescent and photovoltaic device thus is evident. The peaks may also be attributed to the excitonic recombination phonon process near the band edge levels in ZnO.

4. Conclusion
ZnO is a typical II-VI semiconductor with band gap energy of 3.6 eV at room temperature. Optical properties of ZnO nanoparticles have been studied in the past and evidence for its quantum size effect due to nano dimensions can easily be found in literatures. In the present project, ZnO nanoparticles were prepared by a simple cost effective method. The structural analysis of the fabricated ZnO nanoparticles has been done using XRD techniques. The analysis shows that the prepared samples are in the cubic phase of corresponding nanoparticles. The average size of particles, calculated from the Debye Seherer’s formula for the undoped case with respect to most intense peaks (111) and (220) is about 23 nm. The size dramatically decreases with doping to an average of 18 nm increasing the band gap so as to increase the tunability. Also the corresponding strain (ε) and dislocation density (ρ) have been estimated.

It may be also noted that ZnO shows photoluminescent properties in the near ultra violet and visible region making it possible to study the emission properties of nanocrystalline ZnO nanoparticles. The doped variant shows an increase in the photoluminescent emission. The V-I characteristics may be studied which may harness its photo voltaic properties. More optical properties of the synthesized sample may be done which may reveal its optical characteristics such as variation of refractive index with size which can be used for the fabrication of optical waveguides (to be fabricated). By doping ZnO with other metals, it is possible to increase its nonlinear properties and thus it may be used for the production of super luminescence in materials.

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