Sol-Gel Synthesis and Characterization of Pure and Silver Doped Zinc Oxide Nanoparticles

Aravapalli Vanaja, Karumuri Srinivasa Rao

Abstract- ZnO is a fast maturing semiconductor with significant research effort invested in it over the past decade. The emerging novel optical and electronic properties of ZnO semiconductor nanoparticles have been a focusing issue among researchers due to the great prospective in optoelectronic applications including transparent thin-film transistors, photo detectors, light-emitting diodes and laser diodes that operate in the blue and ultraviolet region of the spectrum. To enhance the properties of ZnO, researchers concentrate on doping ZnO with transition metal ions (Al, Cu, Ni).In this paper Influence of Ag doping on structure, morphology and optical properties were investigated. Pure and silver doped ZnO nanoparticles were synthesized by simple, inexpensive Sol–gel process. The powders were investigated using X Ray Diffraction (XRD), Scanning electron Microscopy (SEM) and Fourier transform infrared (FTIR) Spectroscopic characterizations. XRD reveals hexagonal wurtzite structure of nanoparicles with high purity. The incorporation of Ag+ in the place of Zn2+ provoked an increase in the size of nanoparticles as compared to undoped or pure ZnO nanoparticles. SEM images showed that Ag doping has great influence on morphology of ZnO. The presence of functional groups analyzed using FTIR spectra. Ag doped ZnO nanoparticles in the present study have played a vital role in surface morphology, structural and optical properties of ZnO nanoparticles.

Index terms - FTIR, Nanoparticles, SEM, XRD, Zinc oxide

I. INTRODUCTION

Nanoparticles are becoming key components in wide range of applications in engineering, medicine, Pharmaceutical molecular science, medical engineering toxicology, cosmetics, energy, food technology, environment and health diseases. As we enter to the twenty first century, semiconductor nanostructures are revolutnalizing many areas of electronics, optoelectronics and photonics. ZnO nanoparticles are very important in the category of semiconductor nanoparticles. It is an intrinsic n-type semiconductor material that crystallizes in the hexagonal crystal system; it is relatively inexpensive, presents low toxicity, and is very effective in protecting against UV rays. It is attractive due to its wide band gap of 3.4 eV,large bond strength and large exiton binding energy of 60 meV It is also one of the few ceramic oxides that shows quantum confinement effects in experimentally accessible size. Many research groups concentrate on doping ZnO with transition metal ions (Al, Cu ,Ag ,Ni). As transition metal elements have close ionic radius parameter to that of Zn2+, these elements can easily penetrate into ZnO crystal lattice or substitute Zn2+ position in crystal, these are widely used in spintronics, photonics and optoelectronics device applications.

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Aravapalli Vanaja, Department of Physics, Lingaya's University, Old Faridabad, India.

Karumuri Srinivasa Rao, Department of Physics, Lingaya's University, Old Faridabad, India.

Silver is soft, white, lustrous transition metal it possesses the highest electrical conductivity, thermal conductivity and reflectivity of any metal. It is also good for producing a shallow acceptor level in ZnO as it is a soft more over ZnO doped with Ag can improve the distribution of surface charges, accept a conduction band generated by solar light irradiation during photoreaction, prevent the recombination of the photo generated electron-hole., ZnO/Ag has received considerable attention. Many researchers reported that Ag doped ZnO Nanomaterials enhances ultraviolet emission and improves electrical and optical properties (Ruby Chauhan etal, 2010), Photocatalytic and photoluminescence properties, ((Nguyen Van Nghia* et al, 2012) Micro leakage and antibacterial properties (M. Shayani Rad et al, 2013). Since the physical and chemical properties of ZnO nanoparticles are influenced both by their shape and size, a control of morphology of ZnO structures is needed for their commercial usage. ZnO with various nano-sized structures can made using simple fabrication methods including solvothermal, hydrothermal, chemical vapor deposition (CVD), laser ablation, oxidation process, precipitation, gel-combustion, and sol–gel. In the present work sol-gel method is used to synthesize pure and silver doped nanoparticles. The particles were further characterized using X Ray diffraction, Scanning Electron Microscopy (SEM) and Fourier transform infrared (FTIR) to investigate the effect of Silver on structural ,morphological and optical properties of zinc oxide nanoparticles.

II. EXPERIMENTAL PROCEDURE

Chemicals

Zinc chloride (ZnCl2), Sodium Hydroxide (NaOH), silver Nitrate (Ag $(NO_3)_2$) and Ethanol (C_2H_6O) were purchased and used without any purification. The chemicals used are of analytical grade purity.

Synthesis of ZnO, Silver doped ZnO Nanoparticles

The procedure for preparing un doped and Ag doped Nanoparticles is as follows.. To synthesize Pure ZnO Nanoparticles, 0.5 M aqueous ethanol solution of Zinc Nitrate was kept under constant stirring using magnetic stirrer to dissolve completely Zinc Nitrate for one hour and 0.5 M aqueous ethanol solution of NaOH was also prepared in the same way with stirring of one hour. After complete dissolution of $ZnCl_2$, 0.5 M NaOH aqueous solution was added under high speed constant stirring, drop by drop (slowly for 45 min) touching the walls of the vessel. The reaction was allowed to proceed for 2 hrs after complete addition of NaOH. The beaker was sealed at this condition for 2 h. After the completion of reaction, the solution was allowed to settle for overnight further, the supernatant solution was separated carefully. The remaining solution was centrifuged for 10 min and the precipitate was removed.

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Thus, precipitated ZnO NPs cleaned three times with deionised water and ethanol to remove the by products which were bound with the nanoparticles. The solution then dried in an oven at about 60◦*C*.After drying $Zn(OH)_2$ is completely converted to into ZnO. For the synthesis of Ag-doped ZnO nanopowder 0.5 M concentration of silver Nitrate ($Ag(NO_3)_3$) was added into the zinc solution before sodium hydroxide NaOH solution and the same procedure was repeated to obtain the Ag doped ZnO nanoparticles from $Ag(OH)_2$ precipitate. The samples were further characterized.

Characterization

The characterizations were performed to analyze the properties of Nanopowders.The structural Characterization is performed using X Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) The optical characterization is performed using Fourier Transform Infrared spectroscopy (FTIR) .The Confirmation of pure ZnO phase is verified by XRD analysis. The shape and morphology of particles were studied from SEM pictures obtained. Several absorption peaks are observed through FTIR spectrum

III. RESULTS AND DISCUSSION

A. X Ray Diffraction (XRD)

The crystallinity of ZnO nanoparticles were determined by XRD. Figure (a) and (b) represent the XRD pattern of Pure and Ag doped ZnO nanoparticles collected over a 2θ range of 20°-80° using CuKβ radiation. In the Fig[a] ,the distinctive ZnO peaks at 25.356°, 27.314°, 28.90°, 29.712°, 32.22° , 32.822° ,33.346°, 34.76°,35.68°, 39.330°, 42.871°, 48.244°, 58.40° and 66.91° corresponding to lattice planes (1 0 0) ,(0 0 2), (1 0 1) (1 0 2) (1 1 0) (1 0 3) (1 1 2) and (2 0 1) respectively.

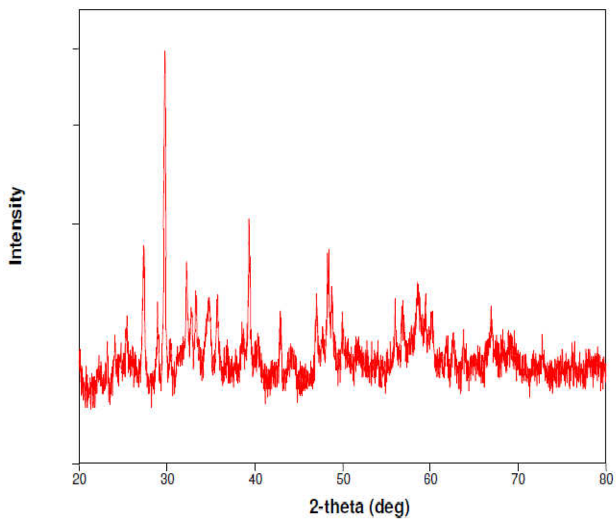


Figure (a) XRD Pattern of Pure ZnO Nanoparticles

In the Fig [b], the distinctive ZnO peaks at 25.356°, 27.314°, 29.90°, 29.712° ,32.224°, 32.822° ,33.246° ,34.6° ,35.68°, 39.330° ,42.861°, 42.244°, 48.68°, 58.40°, and 66.91° corresponds to the lattice planes (1 0 0) , (0 0 2), (1 0 1) (1 0 2) (1 1 0) (1 0 3) (1 1 2) and (2 0 1) respectively . The powders represent well crystalline with Wurtzite hexagonal phase. The broadening shows nanometer range of particles without an impurity phase.

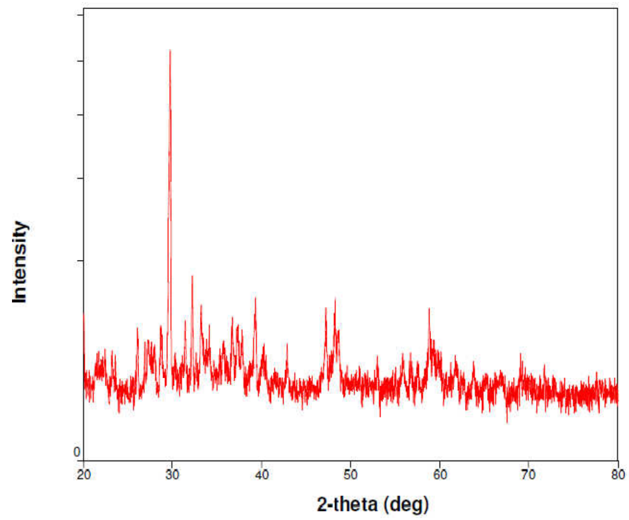


Figure (b) XRD Pattern Of Ag doped ZnO Nanoparticles

The crystallite size D is calculated using the Debye formula:

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

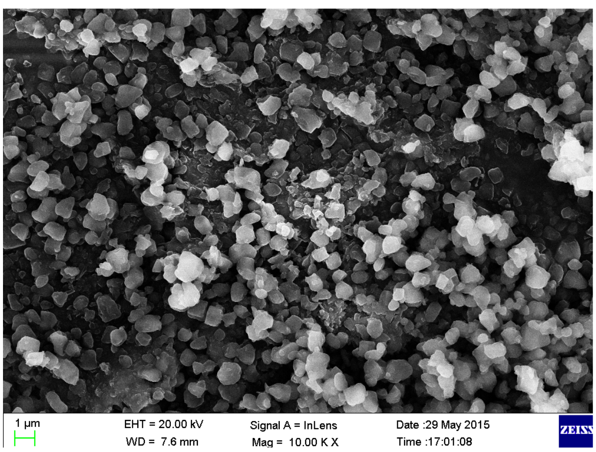
The lattice strain induced in particles calculated using the formula :

$$\varepsilon = \frac{\beta_{hkl}}{\beta \tan\theta}$$

Where λ is X-ray wavelength, β is the peak FWHM of the diffraction peak corresponding to <1 0 1 >, θ is the Braggs diffraction angle

The most intense peak <1 0 1> is chosen to determine the Crystallite size and lattice strain of the nanoparticles.The average crystalline size and lattice strain is found to be 72.17 nm and 0.0020 for pure ZnO nanoparticles and 73.41 nm and 0.0019 for Ag doped ZnO Nanoparticles . The small change in crystallite size and lattice strain was observed due to the incorporation of Ag in ZnO. In addition, the patterns show slight variations in all the diffraction peak positions and lattice parameters in Ag-ZnO nanoparticles compared to pure ZnO. It suggests that Ag has been incorporated into lattice without affecting the overall structure and also the metal deposits on the surface. These results reveal that the molar ratio of OH- to Zn2+ is a dominant factor for the formation of the ZnO nanoparticles.

B. Scanning Electron Microscopy (SEM)



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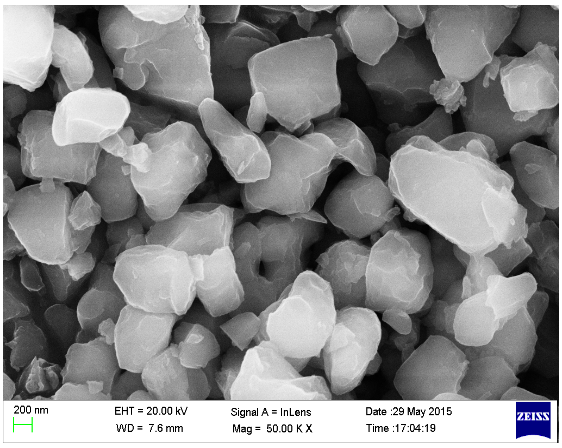
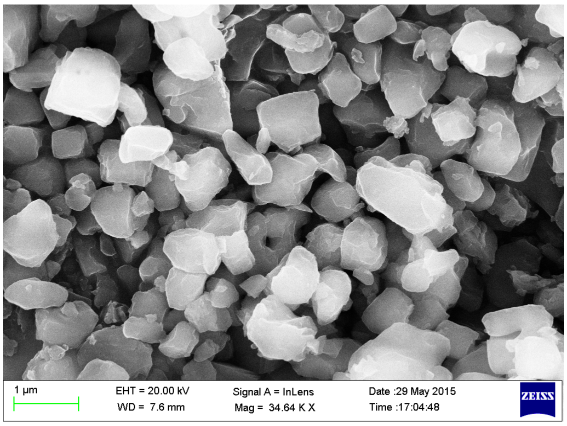
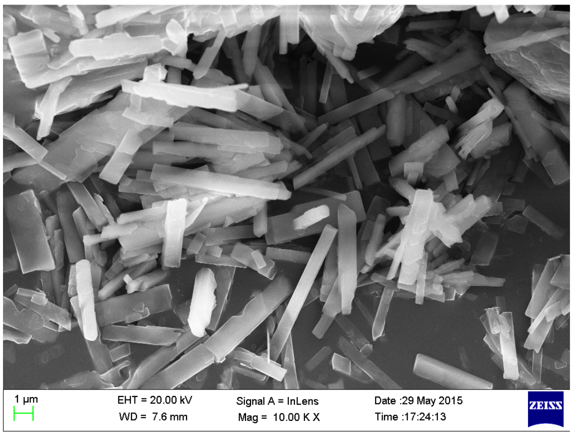
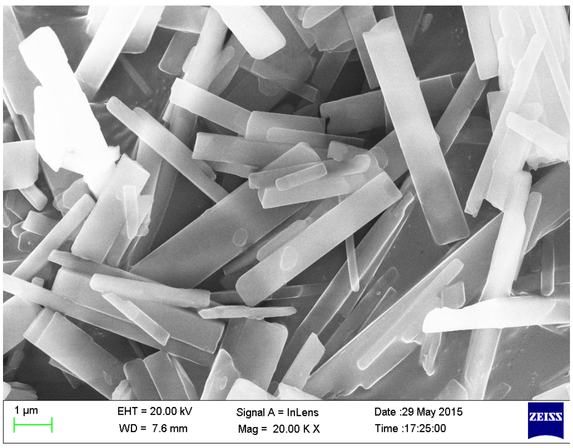




Figure(c) SEM Image of Pure ZnO Nanoparticles





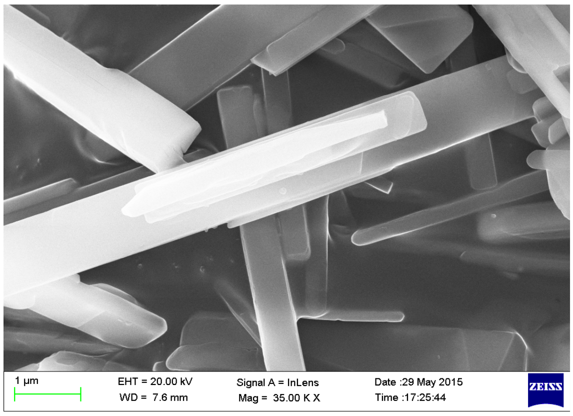


Figure (d) SEM Image of Ag doped ZnO Nanoparicles

The morphology of ZnO Nanoparticles is estimated using SEM .Figure(c) and (d)show the typical SEM micrographs of the pure and Ag doped ZnO Nanoparticles observed at different magnifications. Nano flake like morphology composed of spherical particles were observed in SEM micrographs of Pure ZnO Nanoparticles .Nanoparticles of rod like morphology with better control of size were confirmed from SEM pictures of Ag doped ZnO nanoparticles. From spectra, It is clear that images are well ordered with lower aggregation. The morphology clearly changed with doping.

B. Fourier Transform Infrared (FTIR) Spectroscopy

The formation of Wurtzite structure is further confirmed by FTIR spectra.Various modes of vibration are observed in the FTIR spectra of ZnO and Ag-ZnO Nanoparticles recorded between 3500-1000 cm^{-1}. In Figure (d),the spectrum modes of vibration near 2300 cm^{-1} corresponds to O-H bending vibration. The other peaks in the spectra represent characteristics of the sample .The wide absorption peak near 1500 cm^{-1} indicates CO absorption .The contains broad peaks in the region 3500-3000 cm^{-1} due to the overlapping of O-H stretching modes. The FTIR spectrum shows main absorption band due to Zn-O stretching of ZnO in the range of 1000-400 cm^{1}.Figure(e) represents change in the vibration modes due to influence of Ag .The spectra contains O-H set of vibrations around 3452 cm-1 around 1400 cm^{-1} corresponds to CO.

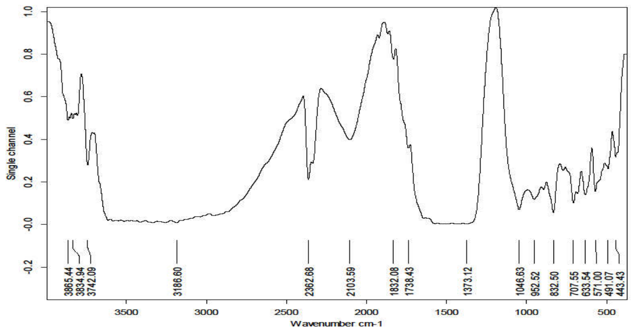


Figure (e) FTIR Spectra of pure ZnO Nanoparicles

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Characteristic absorption band of Ag-O stretching mode is also observed between 580 and 620 cm-1.The sharp peaks represents the high crystallinity of Ag doped ZnO Nanoparticles. The stretching vibrations indicate various deformations. These deformation motions may be (angular changes), such as bending and twisting about certain centers within a molecule also have impact, and contribute to the overall absorption spectrum.

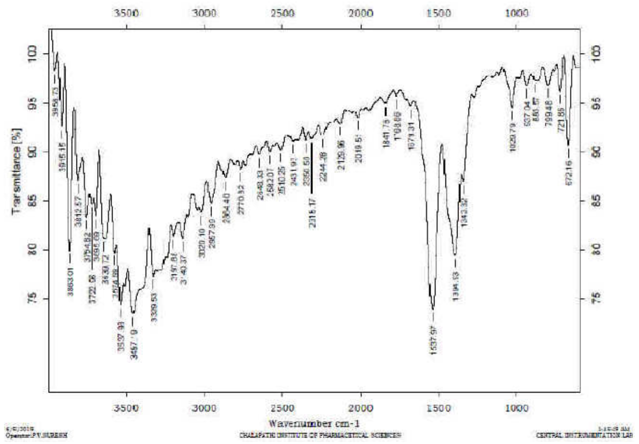

Figure (f) FTIR Spectra of Ag doped ZnO Nanoparticles

IV. CONCLUSION

The Sol gel process used for synthesis of nanoparticles is very simple, cost effective and environment friendly. The future prospects for successful new application in nanotechnology of sol-gel technology depend on the availability of skill researchers able to find out standing obstacles to successful commercial applications which will develop innovative new high performance materials which will in turn create new markets. The nanoparticles could be very useful for the future opto-electronic, photo catalytic and biomaterial applications used in various optoelectronic device applications like solarcells, sensors etc

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