IMPACT OF SILVER DOPANT ON STRUCTURAL, OPTICAL AND ELECTRICAL PROPERTIES OF ZnO NANOPARTICLES

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Pure and silver doped zinc oxide ($Zn_{1-x}Ag_xO$) nanoparticles (NPs) with (x= 0.0, 0.01, 0.03, 0.05 and 0.07) concentration were synthesized by co-precipitation method. The effect of silver concentration on structural, optical and electrical properties of ZnO NPs were investigated using XRD, FTIR , SEM, UV and two probe techniques. The XRD results indicated that pure and Ag-doped ZnO crystalline in hexagonal wurtzite structure and crystallite size varies from 26.99nm~21.44nm. FTIR results shows absorption peaks of pure and Ag-doped ZnO at 417 cm^{-1}, 1550 cm^{-1}, 2360 cm^{-1} and 3750 cm^{-1}. SEM images demonstrated that by silver doping surface became smooth and regular. UV analysis shows that silver doped ZnO NPs shift the absorption edge to red shift and band gap decreases from 3.26 to 3.23 eV. Finally, electrical results indicated that silver doped ZnO NPs shows low resistivity and high conductivity compared to pure ZnO.

1. Introduction

Semiconductor nanoparticles have created much interest among the researchers during the last few years because of their novel optical and electrical properties which shows great potential for many optoelectronic applications [1]. Zinc Oxide (ZnO) is one of the compound semiconductors of the II–VI family with a direct band gap of 3.37 eV at room temperature, and a large excitation binding energy (60 meV). ZnO is low cost and easy to grow. It is also sensitive to the UV region because of its ultra violet absorbance and has high photoconductivity [2]. These properties make ZnO a promising electronic and photonic material shows numerous applications, such as gas sensors , biosensors, biological labels, solar cells, electrochemical cells, varistors, ultraviolet (UV) photodiodes, electrical and optical devices, and surface acoustic wave (SAW) devices [3,4,5].

In Semiconductor technology the chemical, optical and electrical properties of a material can be tuned by using suitable metal dopants has become an important topic. Now a day a lot of research [6–7] has been reported the changes in physical properties of ZnO NPs by using transition metal ions dopants such as Ni, V, Mn, Cu and Ag due to its partially filled d shells which give rise to unpaired electrons. Among these metal elements silver is selected a better choice dopants in ZnO due to its unique properties such as highly conductive, solubility, ionic size and low orbital energy which enhanced its optical and electrical properties. Currently, silver doping in ZnO is strongly suitable for water splitting as photo catalysis, power plant as energy source, dye degradation applications.

A number of methods have been devoted for the synthesis of transition metal doped ZnO nanoparticles, such as auto-combustion method [8], ball-milling method [9], co-precipitation method [10], sol–gel process [11], hydro-thermal route [12] etc. Co-precipitation method is of great interest due to its low cost apparatus, simplicity, lower temperature process and environment

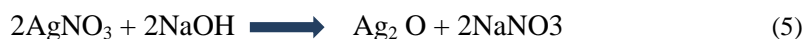---

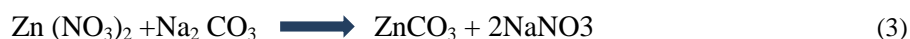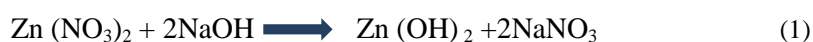*Corresponding author: tariqmunir@gcuf.edu.pk

friendly. In this method reagents are mixed at molecular level consequently there is good control of stoichiometry, purity, homogeneity and morphology.

Even though lot of research work have been carried out on silver doped ZnO NPs [13,14,15,16] but most of the work are on the thin films and the comprehensive study of silver doped ZnO nanopowder is still scanty. Therefore, in the present investigation, the effect of silver (Ag) on structural, morphological, optical and electrical properties of ZnO nanopowder has been studied extensively using x-ray diffraction, scanning electron microscopy, fourier transform infra-red spectroscopy, UV-vis spectroscopy and two probe methods.

2. Experimental procedure

2.1. Synthesis method of silver doped ZnO NPs

Pure and silver-doped zinc oxide powder was synthesized using suitable precursor by co-precipitation method. Aqueous solution of Silver nitrate [Ag (NO)$_3$] and Zinc nitrate [Zn (NO$_3$)$_2$.6H$_2$O] solution is taken in a 500 ml beaker. The other buffer solution of NaOH and Na$_2$CO$_3$ are prepared to maintain pH value of the solution using drop wise in first solution. The solution is heated with continuous stirring for 2 hour. During the reaction, precipitates are formed. The solution filtered and washed by purifying water many times to separate the impurities and then dried at 80°C in an oven. Next the dried samples are grinded and at the end calcination is done for better crystallinity of nanoparticles. The prepared powder was annealed at 600°C for 6 hour inside a muffle furnace. During this procedure following reactions were take place[15].

$$\text{Zn (NO}_3\text{)}_2 + 2\text{NaOH} \longrightarrow \text{Zn (OH)}_2 + 2\text{NaNO}_3 \tag{1}$$

$$2\text{Zn (OH)}_2 + 2\text{NaOH} \longrightarrow 2\text{NaZnO}_2 + 2\text{H2 O} \tag{2}$$

$$\text{Zn (NO}_3\text{)}_2 + \text{Na}_2\text{ CO}_3 \longrightarrow \text{ZnCO}_3 + 2\text{NaNO3} \tag{3}$$

$$\text{ZnCO}_3 \longrightarrow \text{ZnO} + \text{CO2} \tag{4}$$

$$2\text{AgNO}_3 + 2\text{NaOH} \longrightarrow \text{Ag}_2\text{ O} + 2\text{NaNO3} \tag{5}$$

$$2\text{AgNO}_3 + \text{Na}_2\text{CO3} \longrightarrow \text{Ag}_2\text{ CO}_3 + 2\text{NaNO3} \tag{6}$$

$$\text{Ag}_2\text{ O} + \text{CO2} \longrightarrow \text{Ag}_2\text{ CO}_3 \tag{7}$$

3. Results and discussion

3.1. X-ray diffraction (XRD) analysis

Fig.1 shows the XRD pattern of pure and Ag doped ZnO. The diffraction peak of pure ZnO appeared at 2θ values 31.815°, 34.450°, 36.386°, 47.611° and 56.764° are related to (100), (002), (101) (102) and (110) phases of zinc oxide respectively. These 2θ values other than silver are according to JCPDS card of ZnO (00-003-0888). XRD pattern shows hexagonal wurtzite crystal structure (JCPD card no 00-003-0888).The diffraction peaks (111) and (200) appeared at 2θ values 38.195° and 44.289° shows the presence of silver in ZnO lattice and these 2θ values are according to JCPDS card of silver (00-001-1167). It shows the creation of metallic silver (FCC) phase in ZnO. The intensity of silver peaks increases consistent as the concentration of Ag (x= 0.03, 0.05 and 0.07) increases in ZnO. The diffraction pattern of silver doped ZnO does not alter the crystal structure of pure ZnO which shows successful doping of silver.

Table.1 shows that as the silver content (x) increases in ZnO, crystallite size decreases from 26.99 to 21.44nm which is in agreement of [14,15].The Ag dopants in ZnO changes the crystal structure lattice parameters "a" and "c" due to partial substitution of Ag^{1+} ions radius

(0.126nm) to Zn^{2+} ions radius (0.074nm) [16]. However, the volume of ZnO unit cell decreases as an amount of Ag is added which consequently decreases the crystallite size [15, 17].
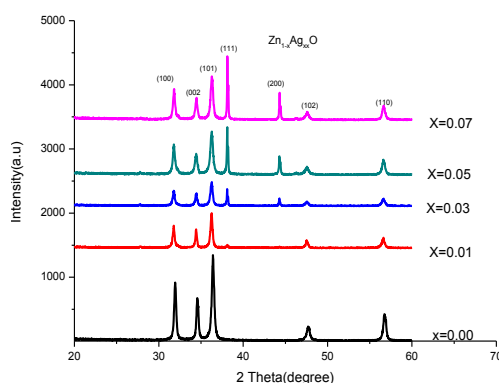

Fig. 1.XRD Patterns of pure and Ag doped ZnO nanoparticles.

Table.1.Geometric parameters of pure and Ag-doped ZnO.

Silver %	Peak Position (degree of 2θ)	(h k l)	Crystallite size (nm)	Parameters		c/a	Unit cell volume(A^0)
				$a(A^0)$	$c(A^0)$		
0.00	36.386	(101)	26.99	3.244	5.200	1.60	47.51
0.01	36.261	(101)	28.84	3.248	5.209	1.60	47.59
0.03	36.269	(101)	22.60	3.248	5.206	1.60	47.56
0.05	36.248	(101)	22.01	3.244	5.200	1.60	47.39
0.07	36.280	(101)	21.44	3.244	5.200	1.60	47.39

3.2. FTIR analysis

Fig. 2 shows the transmittance of pure and silver doped ZnO nanoparticles. It shows the absorption peaks at 417 cm^{-1},1550cm^{-1}, 2360 cm^{-1}and 3750 cm^{-1}. The peak intensities of silver doped ZnO NPs increases which absorb more infrared radiation as compared to pure ZnO. The sharp absorption peak at 417 cm^{-1} which could be due to the stretching vibration mode of Zn-O [18,19].The asymmetric and symmetric bending mode of C=O were in 1410 and 1580 cm^{-1} [15].The absorption peaks observed between 2000cm^{-1} and 2500 cm^{-1} are due to existence of CO_2 molecule formed during the process of making pellet in the air [20]. The absorption peaks at 3020-3650 cm^{-1} that was related to the presence of (OH) ions [15].It is clear that there is no spectra peaks difference of pure and Ag-doped ZnO. Hence, Ag dopants unaltered FTIR spectra of ZnO nanoparticles.
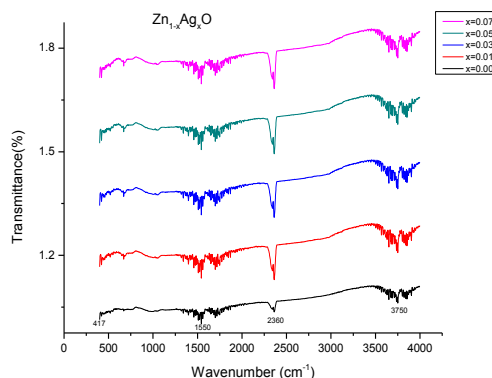

Fig. 2.FTIR spectra of pure and silver doped ZnO NPs.

3.3. Scanning Electron Microscopy (SEM)

Fig. 3(a,b,c,d) shows the surface morphology of pure and Ag-doped ZnO when x=0.00, 0.01, 0.05 and 0.07. SEM analysis indicated that the particles of pure ZnO were non-uniform in size and irregular in shape. While as, the silver content was increased in pure ZnO the particles were obtained with regular shape and uniform size. The concentration of silver also reduced the agglomeration of particles.
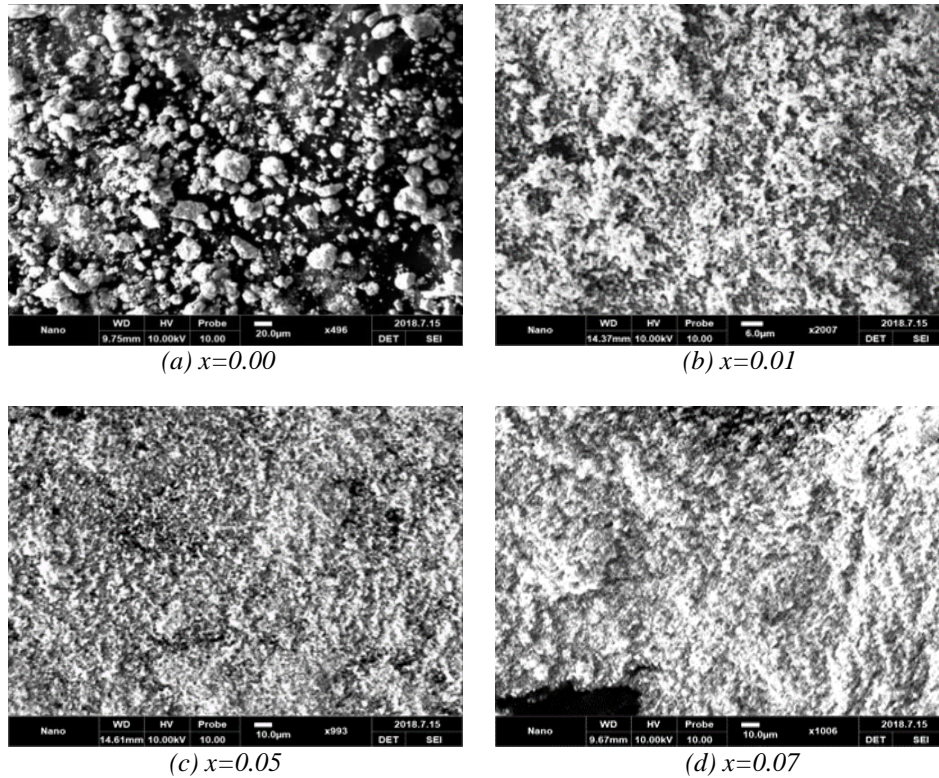

(a) x=0.00

(b) x=0.01

(c) x=0.05

(d) x=0.07

Fig.3.SEM images of (a) Pure and (b) Ag doped ZnO nanoparticles.

3.4. UV-Visible spectroscopy

Fig. 4 shows the UV-vis absorption spectrum of pure and silver doped ZnO NPs. The absorption edge (380nm) of pure ZnO shifted towards longer wavelength (383nm) red shift of silver doped ZnO. The shift in the absorption peak due to silver dopant showed changes in the band structure of ZnO NPs [15].

Fig. 5 shows the band gap of pure and silver doped ZnO NPs. It was found that with increasing the amount of silver (x= 0.0, 0.01, 0.03, 0.05) in ZnO, the band gap decreases from 3.26 to 3.23 eV which is in agreement of [14, 15]. The bandgap decrement due to silver dopant in ZnO NPs showed the potential applications in optoelectronic devices.
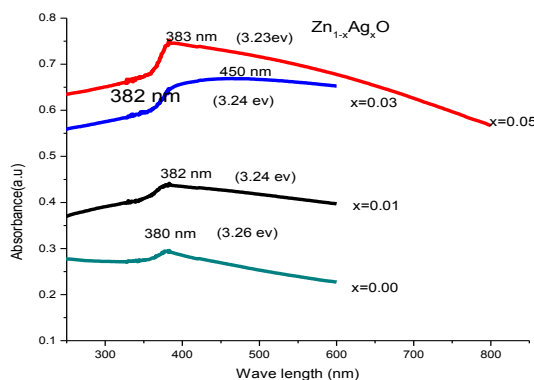
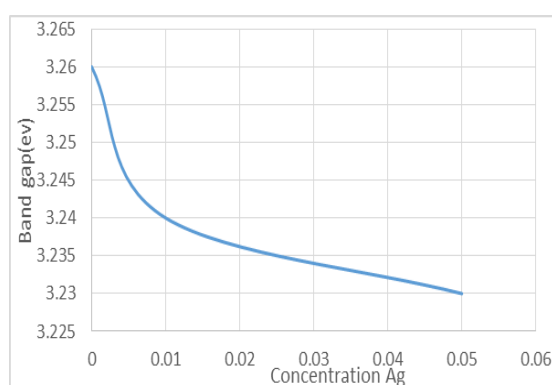*Fig. 4. Absorbance spectrum of pure and Ag doped ZnO.*

Fig. 5. Band gap versus Ag concentration.

3.5. Electrical properties

Fig. 6 shows the resistivity and conductivity of pure and silver doped ZnO NPs. It was found that as Ag concentration (x=0.00, 0.01, 0.05 and 0.07) increases in ZnO, resistivity decreases (7.4×10^8 to 6.8×10^8 ohm-cm) and conductivity increases (1.3×10^8 to 1.47×10^8 ohm-cm)$^{-1}$. It shows that silver ions have substituted Zn^{2+} ions successfully, therefore silver doped ZnO NPs showed better electrical properties which shows its potential applications in electronic devices.
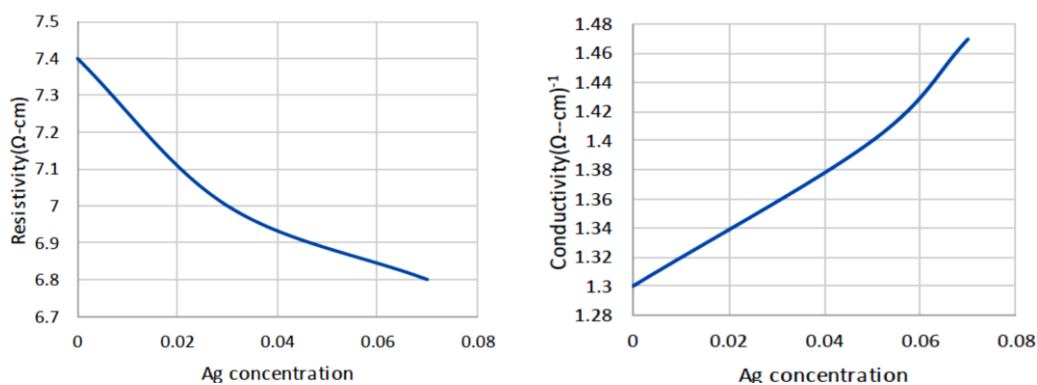

Fig. 6.Pure and silver doped ZnO NPs resistivity and conductivity.

4. Conclusions

Pure and silver doped ZnO NPs were successfully synthesized using co- precipitation method. XRD analysis shows hexagonal wurtzite crystal structure. It also confirmed the presence of silver (FCC) in ZnO NPs. The crystallite size decreases from 26.99~21.44nm. Peaks of FTIR verified that IR spectra of pure and silver doped ZnO nanoparticles were unaltered. SEM results shows that silver-doped ZnO NPs were obtained with the most uniform shape and improved regular size.

UV-Visible analysis showed the red shift in the absorption edge (383 nm) by silver dopant and band gap decreases from 3.26 ~ 3.23 eV. Finally, electrical analysis showed that as the silver content increases in ZnO, resistivity decreases and conductivity increases. It shows that silver ions have substituted Zn^{2+} ions successfully. These results suggested that the silver dopant in ZnO has improved the structural, optical and electrical properties which show potential applications in optical and electronic devices.

Acknowledgement

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