

Influence of metal (Ag, Cd, Cu)-doping on the optical properties of ZnO nanopowder: Variation of band gap

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Abstract

Metal doped ZnO (MZO, metal = Ag, Cd, Cu) with different metal ion doped concentrations were synthesized by sol-gel method. The structural and optical properties were characterized by UV-Vis spectroscopy and Fourier transform infrared (FT-IR). With metal ion doping content increase, a red shift in band gap is observed. The red shift in band edge absorption peak in UV-Vis absorbance spectrum with increasing metal content also confirm the doping of metal in ZnO nanostructure. The band gap of ZnO resistivity was also changed according to the metal doping amounts and a kind of dopant. The results showed that each metal ion that has closer ionic radius to Zn²⁺ could change optical band gap more than other.

Keywords: Band gap, Sol-gel, Nanostructure, Ag-ZnO, Cd-ZnO, Cu-ZnO

1. 1. Introduction

The semiconductor ZnO has gained substantial interest in the research community. The interest in ZnO is fueled and fanned by its prospects in short wave optoelectronics applications owing to its direct wide band gap ($E_g \sim 3.2-3.4$ eV at 300 K [1]) and its large exciton binding energy (~ 60 meV), which could lead to lasing action based on exciton recombination even above room temperature. ZnO is a self-excitation semiconductor, one of the most important promising materials which have been applied to many fields such as transparent conductive contacts, solar cells, laser diodes, ultraviolet lasers, thin film transistors, optoelectronic and piezoelectric applications and surface acoustic wave devices [1-3]. It has high transparency, inexpensive, non-toxic and chemically stable. Its low cost compared with other materials makes it a good candidate for industrial applications. Recently, micro- and nanostructured ZnO has been obtained by using various physical and chemical techniques [4-8]. Also owing to high photocatalytic activity, low cost and environmentally friendly feature [9, 10], ZnO has been widely used as a photocatalyst [11]. However, due to a wide band gap of 3.37 eV, poor photon absorption of ZnO limits its

application in visible light photocatalyst [12]. In order to shift the optical absorption of ZnO into the visible region, one possible approach is to dope transition metal ions into ZnO photocatalyst [13]. Metal-doped ZnO nanomaterials permit tuning of chemical and physical properties by the incorporation of the dopant in lattices of ZnO [14]. The possibility of band gap engineering is reported by Chang et al. in the doped ZnO by the barrier layers which will facilitate radiative recombination by carrier confinement [15]. The control of properties for metal-doped ZnO and band gap engineering of nanomaterials is of utmost importance for tunable light emitting diodes (LEDs) and other optoelectronic devices. Some transition metal elements have close ionic radius parameter to that of Zn²⁺, which means that these elements can easily penetrate into ZnO crystal lattice or substitute Zn²⁺ position in crystal [16]. In this paper, metal (Ag, Cd, Cu)-doped ZnO nanostructures were prepared by sol-gel method. Cd²⁺ and Cu²⁺ have close radius to Zn²⁺. Also, Ag⁺ is a good electric conductor with relatively lower optical absorption coefficient in the visible region, and it is an important optical material in the visible region and the near infrared region. Ag doping in ZnO has been

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reported to be able to change the optical properties of ZnO nanostructure [17, 18]. In this work, the effects of doping level on the optical properties of ZnO nanostructures were studied. The absorption spectra of the samples were measured; the variation of the optical band gap was analyzed.

2. Experimental

2.1. Materials and Instruments

Zinc acetate dehydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$), AgNO_3 , $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, Deionized Water, diethanolamine (DEA), hydroxyl propyl cellulose (HPC) were obtained from Merck and $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ were obtained from Aldrich.

The UV-Vis absorption spectra were measured under the diffuse reflectance mode in the range of 205–1000 nm with a PerkinElmer Lambda 25 UV-Vis spectrophotometer. Fourier transform infrared spectroscopy (FT-IR) analysis was carried out on a Varian model 640 spectrophotometer to determine the specific functional groups present on the surface and impurities of synthesized samples.

2.2. Synthesis

In this work, ZnO was synthesized by the following seven-step reaction:

Step 1: 1.64 g $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ was dissolved in absolute ethanol and stirred for 10 min to get a precursor solution (solution A).

Step 2: 0.05 g hydroxyl propyl cellulose (HPC, $\text{MW} \approx 100000$) was dissolved in 30 ml ethanol and stirred for 10-15 min (solution B).

Step 3: Solution A was added into the clear solution B. The resulting solution was stirred for 10 min at 60 °C (solution C).

Step 4: A mixture of 0.15 mL deionized water, 0.85 mL diethanolamine (DEA), and 5 ml ethanol was stirred for 10 min. The molar ratios of diethanolamine/zinc acetate were 1:1 (solution D).

Step 5: $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Ag}(\text{NO}_3)$ or $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ were added into the solution D to obtain the different molar ratios of doped metal (Cd, Ag or Cu)/Zn (0, 0.02, 0.05, 0.1) and stirred for 10 min (solution E). Step 6: solution E was then dropped into the precursor solution C, at speed of one drop per second under a strong stirring. After that, the solution was continuously stirred for 30 min to achieve a transparent ZnO sol. Step 7: The obtained transparent sol was then aged for 20 h in air at room temperature and was subsequently dried in water bath at 65 °C for 4 h and in oven at 80 °C for 3 h and was finally calcined at 400 °C for 2 h in a furnace. The detailed preparing process is shown in Fig.1.

3. Results and discussion

3.1. Ultraviolet-Visible spectroscopy

UV-Vis spectroscopy was performed to examine the optical properties of synthesized ZnO, ZnO:Ag, ZnO:Cu and ZnO:Cu (nanoparticles) at room temperature and result is reported in Fig. 2. The different synthesized ZnO (nanoparticles) exhibit a single and well-defined absorption band at 377 nm, which is the characteristic band for the wurtzite hexagonal structure of ZnO [19]. The obtained UV-Vis spectrum for ZnO:dopant nanostructure does not show any significant change in the absorption spectrum due to the doping of Ag, Cd and Cu into ZnO lattices. The wavelengths of maximum absorbance for each nanostructure sample are listed in Table 1. The observed results are almost similar with the already reported literature [20]. The band gap energy of nanostructure(s) were calculated from $(\alpha h\nu)^2$ vs. $h\nu$ plot, where α is the optical absorption coefficient from the absorption data and $h\nu$ is the energy of incident photon. The band gap energy (E_g) was estimated by assuming a direct transition between valence and conduction bands from the following expression [21]:

$$\alpha h\nu = K(h\nu - E_g)^{1/2} \quad (1)$$

Where K is a constant and the intercepts of these plots afford an estimate of the optical band gap energy of the corresponding samples as shown in Fig. 3. Band gap value of 3.02 eV is obtained for pure ZnO nanostructure while the band gap of ZnO:Ag, ZnO:Cu and ZnO:Cu nanostructure samples was found to decrease upon increasing. Metal (Ag, Cd and Cu) dopant concentration (0, 2, 5 and 10 mol.%) as presented in Table 1. It can be observed, that the band gap (E_g) of ZnO can be tuned over a large energy range using the doping process. Interestingly enough, the E_g value of the doped ZnO is lower than that of pure sample. This is due to the formation of Zn-O-M bonds between metal dopant and ZnO. A similar result was also reported for ZnO:Cu [22], ZnO:Ag [4] and ZnO:Cu [23]. When metal dopant ions were added into the ZnO nanostructure, E_g red-shifted from 3.02 eV to lower E_g value. A significant change of E_g value with an absorption peak in longer wavelength was found for the ZnO:M. Note that an associated increase in the band gap with a decrease in particle size is an indication of the quantum confinement effect [24]. The variation of the red-shifts of E_g with an increase of metal dopant content has been suggested to be due to the increased number of sp-d exchange interactions between the band electrons and the localized d electrons of metal dopant ions [25]. It is very likely that the metal dopant acts as an ionized donor, providing ions and introducing deep states in the band gap. When metal dopant ions substituted Zn sites in the ZnO lattice, the band gap narrowed due to sp-d exchange interactions between the conduction band (made up of the 4s4p orbital of Zn) electrons and the d electrons of metal dopant ions (Cd, Ag and Cu).

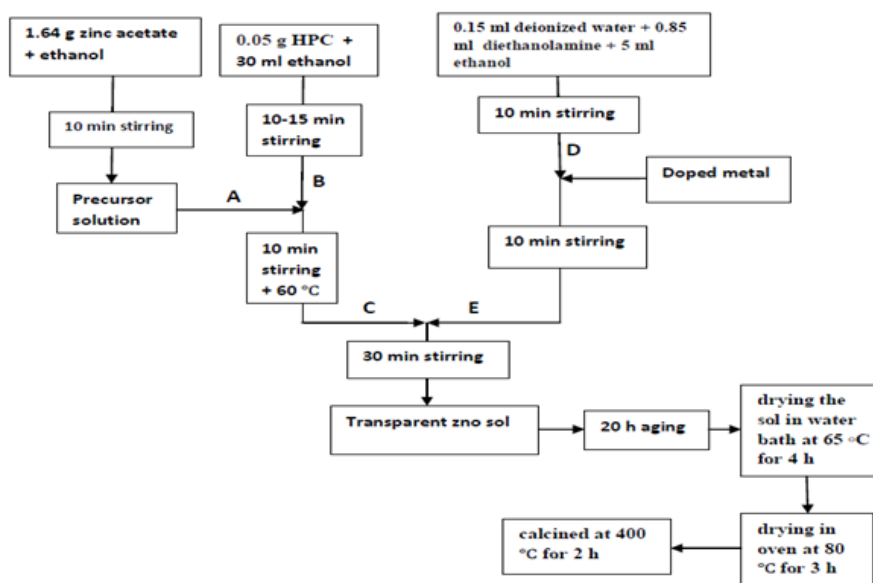


Figure 1. Flowchart of the preparation process of the doped ZnO:M nanostructures

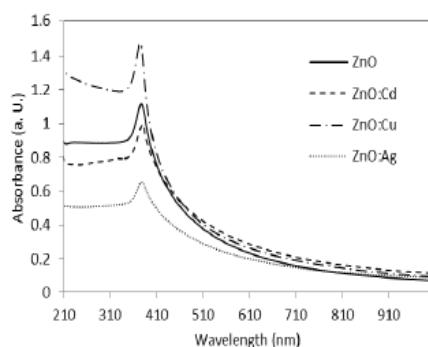
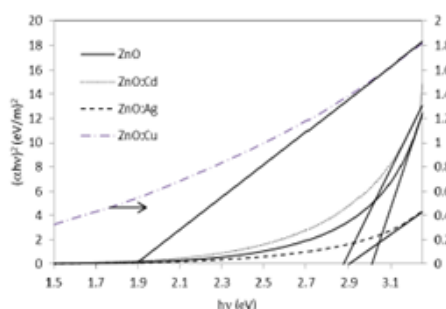


Figure 2. UV-Vis spectrum of ZnO nanostructure and different doped ZnO:M.

Figure 3. Plots of $(\alpha hv)^2$ versus energy ($h\nu$) for ZnO, ZnO: Cd, ZnO: Ag and ZnO: Cu nanostructure with 10% mole dopant metal.

Increasing the concentration of dopant ions concentration cause the development of a resonance structure in the density of states. This development also causes the split off band. The narrowing band gap energy is possibly due to the existence of dopant metal ions impurities in the ZnO structure, which induce the

formation of new recombination centers with lower emission energy. On the other hand, it is demonstrated that the band gap is narrowing with increasing dopants content.

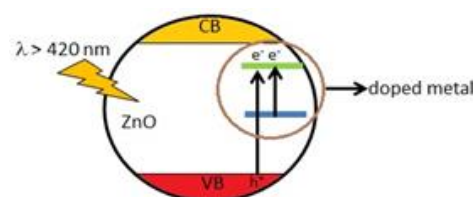


Figure 4. Schematic diagram of photoexcited electron-hole separation process.

The main reason is that the Ag^+ , Cd^{2+} or Cu^{2+} ions substitute the Zn^{2+} ions. The substitution by the Cu^{2+} (0.73 \AA) ions of less radius than that of the Zn^{2+} (0.74 \AA) leads to the more decrease of optical band gap rather than by larger Cd^{2+} (0.97 \AA) and Ag^+ (1.26 \AA) ions at the similar amount of dopant (Table 1). We see that, since Cd^{2+} ion radius is closer to Zn^{2+} ion radius, compared to Ag^+ , the optical band gap in ZnO: Cd decreases more than that in ZnO: Ag. Figure 3 shows the variation of the optical band gap as a function of Ag, Cd and Cu content.

Schematic diagram (Fig. 4) represents the proposed mechanism for the narrowing band gap energy due to the possibility of the existence of dopant metal ions impurities in the ZnO structure.

3.2. Fourier transform infrared spectroscopy

The quality and chemical composition of metal doped (Ag, Cd and Cu) ZnO nanostructures were investigated by FTIR spectroscopy at room-temperature in the range of $400\text{--}4000 \text{ cm}^{-1}$ and demonstrated in Fig. 5. Several absorption peaks at

475, 891, 1623 and 3425 cm^{-1} were observed in the obtained FTIR spectrum. The absorption peak appeared at 3425 cm^{-1} is related to the O-H stretching mode [25]. Very small peaks originated at 891 cm^{-1} is probably due to the nitrate (NO_3^-) groups [26]. Appearance of another small absorption peak at 1623 cm^{-1} could be ascribed to the bending vibration of absorbed water and surface hydroxyl [25]. Except the above mentioned absorption bands, no other distinguished peak related to any other functional group is detected in the FTIR spectrum, which clearly reflects that the synthesized product has no significant

impurity. Fig. 5 shows the FT-IR spectra of Ag, Cd and Cu doped ZnO, which are almost similar to that of the ZnO nanostructure. The vibration mode at wave number 475 cm^{-1} changes slightly, because of ionic radii mismatch between Ag^+ , Cd^{2+} , Cu^{2+} and Zn^{2+} ion [27]. All the peaks are slightly shifted due to the effect of doping in metal-doped ZnO nanostructures, and this effect should owe to an interaction between ZnO and metal ions for formation of new bond.

Table 1. Characterization of different synthesized ZnO nanostructures.

Number	Nano Compound	Mole % dopant metal	Band gap (ev)	Wavelength (nm)	WaveNumber (Cm^{-1})
1	ZnO	-----	3.02	376	475
2	Ag-ZnO	2	2.83	377	472
3	Ag-ZnO	5	2.9	377	475
4	Ag-ZnO	10	2.9	377	478
5	Cu-ZnO	2	3.1	374	472
6	Cu-ZnO	5	2.4	377	461
7	Cu-ZnO	10	1.9	382	458
8	Cd-ZnO	5	2.95	382	475
9	Cd-ZnO	10	2.88	382	478
10	Cd-ZnO	20	2.6	383	475

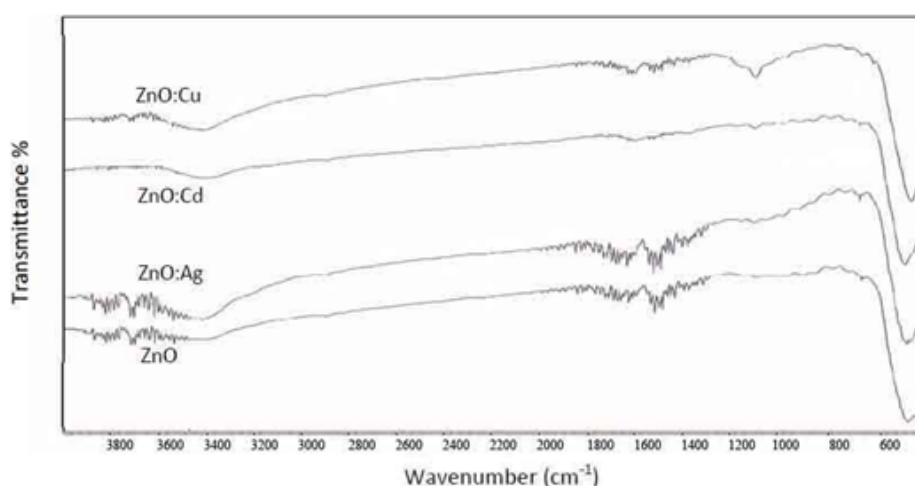


Figure 5. FTIR spectra of different ZnO:M nanostructures.

4. Conclusion

Various undoped/(Ag, Cd, Cu)-doped ZnO nanostructures were synthesized via a simple controllable sol-gel method. The content of metal-doped in the ZnO nanostructures was around 2, 5, 10% mole. The E_g value of the doped ZnO is lower than that of the pure sample. The optical properties of nanostructure samples depended on a type of and a content of dopant in target. Doping Cu in ZnO has most effect in changing band gap value. Increasing

amount of silver to ZnO Structure, cause to decrease band gap value until 5% [Ag^+]/[Zn^{2+}] and upper value of Ag doesn't have any effect on band gap value.

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