Chemically synthesized nano composite (Zinc/Magnesium) Oxide for tunable band gap devices

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Abstract. Formation of heterostructures in nanostructured materials is essential for their potential applications in nano electronics and photonic devices. As a promising candidate for blue and ultraviolet optoelectronic devices, ZnO has attracted much attention due to its wide band gap (3.37eV), large exciton binding energy (60meV), low epitaxial growth temperature and high oxidation resistance. In addition since the ionic radii of Mg\(^{2+}\) (0.57Å) and Zn\(^{2+}\) (0.60Å) are quite close, they may alloy by replacing each other in the matrix. The doping of Mg in ZnO is done through a simple and novel technique from metal acetates using ammonium carbonate as precipitant. An organic capping agent (EDTA) is used prevent agglomeration and the addition is done under constant stirring. The carbonate precursor obtained is heated on the basis of TGA to obtain the metal nano composite. The effects of different parameters on particle size and morphology of (Zn-Mg)O nano composite is optimized by “one at a time” method. Under optimum conditions, spongy shaped, uniform and homogeneous structured (Zn-Mg)O nano composite powders with particle size few nano meters are obtained. The optical and structural properties of nano composite prepared by solution techniques are investigated by X-ray diffraction, UV-Visible spectroscopy, and PL, FTIR and electron microscopy techniques. The effect of annealing on the optical properties of this nano composite is also studied

1. Introduction

During the last few years, synthesis of nanostructured metal oxide has been attracted considerable attention due to its wide range of applications and important properties owing to large surface to volume ratio. ZnO nanoparticles have wide range of application in solar cells, catalysts, gas sensors, luminescent devices etc. There are a number of methods to prepare nanoparticles and composites. In recent years, researchers have focussed more on the synthesis of both nanoparticles and nano composite of ZnO and MgO due to their application in advanced technologies. Various synthesis methods have been in use for making nanostructured metal oxides and its composites [1-6]. The (Zn-Mg)O Nano composites were also prepared using different techniques using different metal salts as starting material but most involving costly atmosphere and need high temperature. Here we suggest a
simple room temperature routine using aqueous solutions of mother chemicals to make porous and spongy Nano structured ZnO,MgO and their composite.

In the present work a wet chemical method is used for preparing nano composite and nano metal oxides. Metal acetates and ammonium carbonates were used as starting materials and EDTA was used to prevent agglomeration to obtain homogeneous structure.

The TGA analysis was performed in the temperature range from 280°C to 800°C at a heating rate of 150°C/minute under nitrogen. The surface morphology of the powdered sample was obtained by scanning electron microscope (SEM) [JEOL/EO JSM-6390] and the chemical composition were found out using the energy dispersive analysis of X-rays(EDAX). XRD study was carried out using XPERT-PRO model powder diffractometer (PAN analytical, Netherlands) employing Cu- Kα radiation (λ = 1.54060Å) operating at 40kV,30mA and the optical properties were analyzed using UV–Visible analysis, FTIR and PL analysis.

2. Experimental methods

2.1. Materials used and apparatus

Analytical grade Zinc acetate dehydrate, Magnesium acetate dehydrate, ammonium carbonate EDTA and Sodium hydroxide were obtained from MERCK. All solutions were made in distilled water in different molar concentrations and the whole precipitation technique was done by slow addition under constant stirring using a magnetic stirrer. The pH of the solution was adjusted using sodium hydroxide to aid precipitation. The obtained metal carbonate precursor was washed several times with distilled water, filtered, dried and ground thoroughly to obtain fine powders.

2.2 Results and discussion

Analysis of TGA and derivative of TGA curve show a considerable weight loss in the temperature range 300°C to 450°C , the maximum weight loss being near 400°C for all the samples. So the decomposition temperature was taken as 500°C to convert the carbonates into oxides.

In the present study samples are also sintered at 700°C and 900°C to understand the effect of annealing on the structure and optical properties of these nano metal oxides. Figures 1(a),1(b) and 1(c) depicts EDAX of ZnO,MgO and ZnO/MgO and they show that the samples are free from impurities. Figures 2(a), 2(b) and 2(c) are SEM micrographs and they show the morphology of the samples. The magnesium oxide nanoflakes can be seen in Fig 2(b). The other two shows spherical morphology.
The XRD spectrum of the samples (given in Fig 3 a,3b, and 3c) reveals that all the oxides are crystalline. The fine particle size is detected in X-ray line broadening. The particle sizes of both samples determined using the Scherrer equation and found that size of particles are of few nm ranging from 8~15nm and the particle size increase with temperature due to agglomeration. The XRD spectra of samples are compared with JCPDS data, and the lattice parameters are calculated. The obtained values are found in good agreement with JCPDS values (ZnO- card no079-0205, MgO-Card no 03-0998). The peaks of the composite itself is a proof for the presence of Mg in ZnO lattice.

UV spectrum of the three samples is shown in figure 4 and the absorption peak of composite shows a small blue shift as compared to that of pure ZnO which clearly shows that the bandgap increases due to the doping of Mg. The peak value of absorbance are used to find the band gap which were obtained as 3.487eV for ZnO, 4.824eV for MgO in the nano forms and 3.624eV for the nano composite.
The bandgap of nano semi conducting metal oxides are found to be size dependent and can be increased slightly by reducing the size even though within limits. But controlling the size of nanoparticles through controlling the parameters in the synthesis method is very difficult. As an alternative the bandgap can also be varied by doping with suitable metal oxides. The luminescence spectrum obtained contains a broad UV emission at 350nm as well as a wide green to red band. The nature and shape of the luminescence spectra also varied with doping. We can also see the changes in the peak intensity caused due to doping. The UV emission is originated from excitonic recombination corresponding to the near band-gap emission of ZnO, while the emission bands in the visible range are due to the recombination of photo-generated holes with singly ionized charge states in intrinsic defects such as oxygen vacancies, Zn interstitials, or impurities \[5,8,9\]. The FTIR diagrams(Fig 6a,6b and 6c) show stretching and bending bands of OH bands attached to metal ions and to the surfaces. There are two types of OH bonding present in this spectra. First is the OH stretching and bending bonded with Metal ions and secondly, OH stretching and bending attached to the surface of the samples. The OH stretching bonded with Metal ions will be appeared as a sharp peak at 3702cm\(^{-1}\), bending bond at 1490cm\(^{-1}\). For the second O-H stretching appears as a broad band at 3600-3200 cm\(^{-1}\) while bending at 1639cm\(^{-1}\). These bands have been characterized by many researchers \[7\].

\[\text{Figure 6a FTIR spectrum of ZnO} \quad \text{Figure 6b FTIR spectrum of MgO} \quad \text{Figure 6c FTIR spectrum of composite}\]

3. Conclusion

The nanocomposite ZnO/MgO and nano ZnO,Nano MgO are prepared using chemical co precipitation technique and there surface morphology and optical properties are studied. This nano powders were characterized by EDAX,SEM ,XRD,FTIR,UV-Vis spectroscopy and PL studies. The band gap, particle size and emissions are studied with doping. FTIR analysis are also done to have a deep insight about the structure. This study confirms the well reported nano size effect and the fact that the band gap can be properly tuned by changing the stoichiometry of (Zn-Mg)O.

Acknowledgement –The first author acknowledges UGC for financial assistance and STIC Cochin, NIST Trivandrum for providing SEM and XRD facilities.

References

[1] Yang Y, Chen H, Zhao B and Bao X 2004 J.Cryst. Growth. 2639 447
[2] Hong Y C and Uhnm H S 2006 Chem.Phys Lett. 422 174
[3] Choi H S and Hwang S T 2000 J. Mater. Res. 15(4) 842-845
[4] Li Y B, Bando Y and Sato T 2002 Chem Phys Lett. 359 141.
[5] Kim T W, Kazawoe T, Yamazaki S, Ohtsu M and Sekiguchi T 2004 Appl. Phys. Lett. 84 3358.
[6] Sunder Manoharan S and Arora Sonia 2009 "Photoluminescent properties of Mg doped ZnO by microwave combustion and microwave polyol method", Mat sci and eng b162:68-73.
[7] Regragui M., Addou M, Outzourchi A, Bernede J C, Eldrissi E, Beneseddk E and Kachouane A 2000 Thin solid films. 358 40
[8] Qiu Z and Wong K S 2004 Appl. Phys. Lett. 84 2739.
[9] Look D C 2001 Mater. Sci. Eng. B 80 383.