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Structural and Optical Properties of ZnS:Cu Transparent Nanosheets

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Abstract

Semiconductor quantum dots based on luminescent properties of II-VI groups' elements have attracted special attention to research community due to their fascinating optical and electronic properties. In this work the colloidal solutions as well as thin films on glass substrates of ZnS and ZnS: Cu in PVA (Poly-Vinyl Alcohol) matrix have been prepared through chemical route. The XRD patterns of the as-prepared sample show a mixed type structures comprising both cubic zinc blende and wurtzite hexagonal phases both for ZnS and ZnS:Cu. The crystallinity is improved on Cu doping with presence of clear broad peak with enhanced intensity. Transmission Electron Microscope (TEM) images exhibit the solid triangular shaped nanostructures for undoped ZnS whereas it shows a multiple transparent nanosheets on copper doping. The surfaces of the assembled triangular solid in fact consist of irregular quantum dots distribution having average size of 5 ~ 8 nm. The UV_VIS spectra of ZnS and ZnS:Cu show a band gap of 4 eV and 3.9eV respectively indicating a significant blue shift from its bulk of band gap energy of 3.7eV. A small red shift of band gap as well as blue luminescence on 1% Cu doping indicates that the dopant atoms exist in an interstitial sites.

Keywords: ZnS:Cu; PVA; CBD; Nanosheets.

Introduction

Metal doped II-V class semiconductors have been attracting a lot to the scientist community because of their self assembled different type nanostructures[1]. This kind of nanomaterials exhibit luminescence properties as the impurity ions largely influence the properties of nanomaterials[1.2.3]. Exploitation of newer properties, therefore provide opportunities to these metal doped nanostructures for their use in different light emitting devices[1.4.5]. Hence more emphasis was given to produce well ordered nanostructures by changing either the growth condition or process of doping in recent years. ZnS is a wide band gap semiconductor material (E_g ~3.6 eV) and is used as phosphor in electroluminescence and opto-luminescence devices[2.3.6]. These materials behave remarkably different from the bulk due to quantum confinement effects[3.5.6.]. On doping different metals into a nanosized ZnS matrix has made this a more vigorous[1] and attractive material because of the alteration of its shape and size with metal doping and such composite nanomaterials have great potential in the application of electro-optic device fabrication such as solar cell, light display devices and other optoectronic devices[1.4.5]. Moreover luminescence characteristic of impurity-activated ZnS nanocrystals differ significantly from those of the bulk ZnS[3.5.6.]. So our effort is dedicated to the synthesis and characterization of ZnS and ZnS:Cu nanostructures. Synthesis of nanoparticles by chemical methods is quite easy and inexpensive as compared to other methods. Keeping the above aspects of applications in light emitting devices and display systems, synthesis of ZnS and of Cu doped ZnS nanophosphors has been under taken in the present work.

Material and Methods

Synthesis: The chemical bath deposition (CBD) method was employed to deposit Cu doped ZnS thin films on to glass substrates[7]. The deposition was carried out in a matrix solution and thiourea. The matrix solution was prepared by adding sulfide ion source and zinc sulphate as zinc ion source in alkaline bath. The aqueous solution of 3% weight of polyvinyl alcohol (PVA) with constant stirring at constant temperature was maintained for overnight. $ZnSO_4$ of (0.5 Molarity) was used to get matrix solutions and equal volume of thiourea solution of same molarity was prepared. Equal volume of the matrix solution and thiourea were mixed together to form ZnS and simultaneously $CuSO_4$ solution of 0.005 morality were added as doping agent to get the Cu doped ZnS thin film. Ammonia solution was added slowly to metal salt solution to form the metal complex and its P^H value was adjusted between 10 and 12[7].

Substrate cleaning plays an important role in the deposition of the thin films[6]. Commercially available glass micro slides of dimensions 26 x 76x2mm were boiled in chromic acid and dried in air prior to deposition. These glass substrates were kept immersed vertically in the as-prepared colloidal solution of nanoparticles for nearly 24 hours at room temperature for deposition of the thin films.

Characterizations: The structural investigation of ZnS and ZnS:Cu was carried out using X-ray powder diffractometer (Model: Seifert XRD 3003 T/T) with CuK_α radiation (λ =0.15406nm) scanning 2θ in the range 20^0-80^0. The morphology of the nanoparticles were characterized by transmission electron

microscope (TEM) [Model: JEOL JEM 100CX-II] operated with an acceleration potential of 100 kV. The UV-Visible absorption of the samples was recorded using an automated spectrometer (Model: HITACI 113210) in the wavelength range 200nm -800nm.

Results and Discussion

The physical appearance of ZnS and ZnS:Cu films deposited at room temperature by CBD indicate that layers are smooth, homogeneous, dirty white in colour and partially transparent and strongly adherent to the substrate. The thin films were taken for XRD characterization while the solutions were taken for TEM and optical studies.

Structural Studies: The XRD patterns exhibit both type of phases which are zinc blende and hexagonal wurtzite for both undoped and Cu doped ZnS nanostructures[2]. The figure-1 (a) and figure-1 (b) show the XRD traces of ZnS and ZnS: Cu respectively. The prominent peak positions (2θ) of undoped ZnS are found at 29^0, 33^0 , 47.3^0 and 58.9^0 corresponding to planes (111) ,(200), (220) and (222) for cubic zinc blende phase while the relatively low intensity peaks at 26.5, 28 and 47.3^0 are assigned to (100), (002) and (110) planes of that of hexagonal type. It is observed that in a mixed type phases of ZnS the crystal planes (111) cubic is close to (002) hexagonal as well as that of (220) is close to (110) and thereby it is often difficult for precise identification. Similarly the XRD peaks of ZnS:Cu are observed at 28.5^0, 32.95^0 and 58.8^0 and their respective cubic planes are (111), (200) and (222). The hexagonal planes are (002) and (110) which corresponds to (2θ) at 27^0 and 47.3^0respectively. A comparison between our data with standard data from JCPDS [No 39-136] clearly shows that both ZnS and ZnS:Cu nanocrystals obtained in this study have the mixture of cubic and hexagonal structure[1.5]. The broadening of the different peaks of the nanoparticles is obviously the characteristic of nanosized particles[6.7]. As compared to the undoped ZnS, the Cu doped ZnS exhibits higher diffraction intensity with well developed different peaks indicating improved crystallinity. The crystallinity is improved in ZnS:Cu because of more and more atoms oriented well for the formation of transparent nanosheets which has been confirmed by TEM morphology. The broaden high intensity peak position at 58^0 (2θ) in ZnS:Cu may be the signature of the Cu element incorporated in ZnS specimen[8]. The estimated sizes of ZnS and ZnS:Cu nanophosphors from XRD using Debye Scherrer formula are found to be 5nm and 7nm respectively. Other peaks are also observed due to presence ZnO and PVA in the samples because of oxidation of Zn^{2+} in PVA and aqueous medium during synthesis process.

Figure-2 (a, b, c, d) display the TEM images of ZnS nanoparticles at different resolution while figure-2.(e. f) represent that of ZnS: Cu nanoparticles. Figure-2(a - b) show 3D triangular shaped ZnS nanostructures. The high resolution TEM image [figure-2 (c)] reveals the surfaces of the solid triangles consist of some spherical particles. A close observation of those well defined particle distributions reveals the formation of irregular quantum dots having average size of 7nm which is close to the average size measurement from XRD. Moreover the figure-2(d) of TEM image at higher resolution shows that the surface also contains lattice defects. Lattice defects may be attributed to the Zn interstitials vacancies and sulfur vacancies due to dangling bonds[5.6].

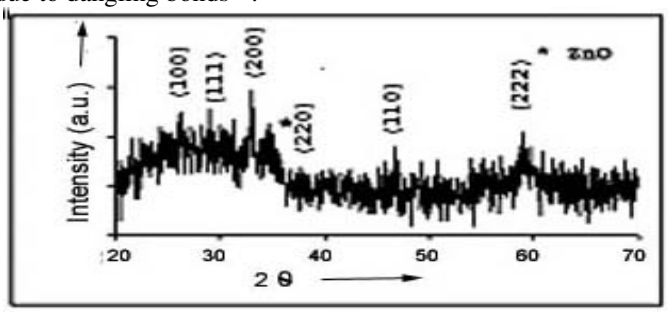

Figure-1(a)
XRD pattern of ZnS

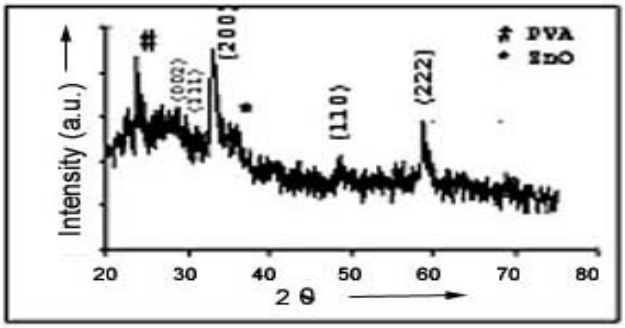

Figure-1(b)
XRD pattern of ZnS:Cu

Figure-2(e) exhibits the formation of well defined multiple 2D nanosheets on copper doping. The nanosheets are quite transparent as seen clearly in the TEM image. ZnS possesses a variety of shape oriented nanostructures depending on its growth conditions. More often anisotropic growth pattern is found in a mixed crystal system. The difference between the two phases is the sequence of atomic layer stacking parallel to the (111) for cubic or (001) for hexagonal planes in the forms of ABCABC..... or ABAB..[9.10]. The theoretical and crystal habit of ZnS growth direction is mostly along hexagonal c-axis in this system[10]. The ZnS nanosheets were formed because of growth of ZnS nuclei along (001) direction. The copper is found to act as catalyst to form nanosheets. Daniel Moore *et al* and other workers also reported the synthesis of similar type of nanosheets and nanobelts of ZnS and ZnS:Cu[5.11]. This author had also found earlier the formation of nanosheets on Cu doping which implies the reproducibility as well as stability of the nanostructures[7]. Figure-2(f) indicates a few isolated nanoparticles and clusters showing an interesting sequence of the assembly events between individual nanoparticles. These observed nanoparticles are of different shape and size due to the different growth mechanisms involving Ostward Ripening (diffusion/dissolution) based coarsening by the surface precipitation of solvated atoms[12].

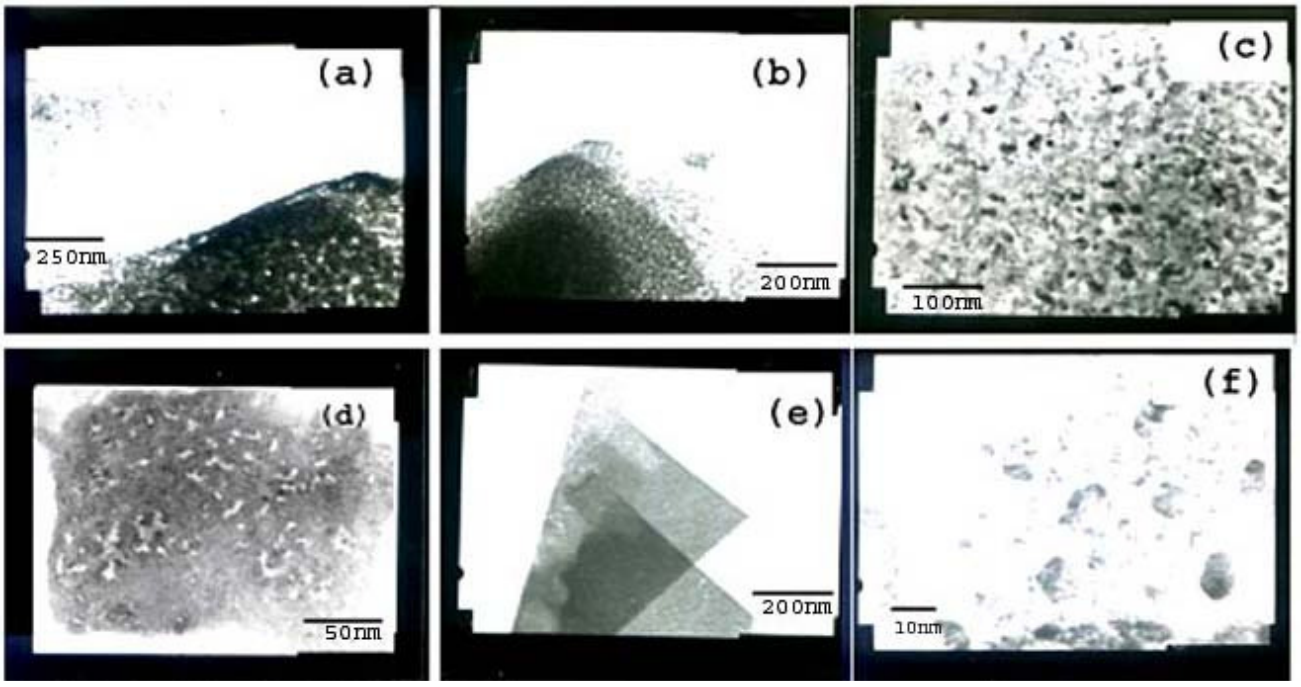

Figure-2 (a, b, c and d)
TEM images of ZnS thin film in increasing order of their resolution and Figure-2 (e and f) TEM images of ZnS:Cu in increasing order of their resolution

Optical properties: The figure-3(a) and figure-3(b) show the UV _Visible spectra of ZnS and of ZnS:Cu nanoparticles respectively. In case of ZnS nanoparticles the absorption peak is observed around 306 nm indicating band gap enhancement due to quantum size effect[6]. In a quantum confinement regime the electrons in the conduction band and the holes in the valence band are spatially confined by the potential barrier of the surface. The lowest energy optical transition from valence band to conduction band increases because of confinement of both electrons and holes. The estimated band gap energy found to be 4.04eV which is quite higher than its bulk band gap energy ~ 3.6eV. The additional absorption at 365nm is owing to inherent native defects. In Cu doped ZnS the UV_Visible spectra reveal the absorption edge at 310 nm indicating red shift and its band gap energy is estimated to be ~ 3.9 eV.

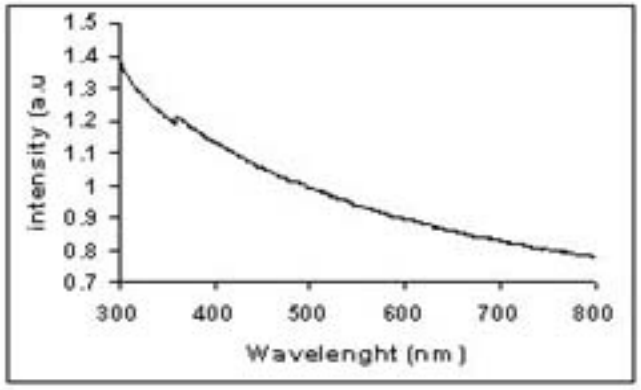

Figure-3(a)
UV_Vis. Spectra of ZnS

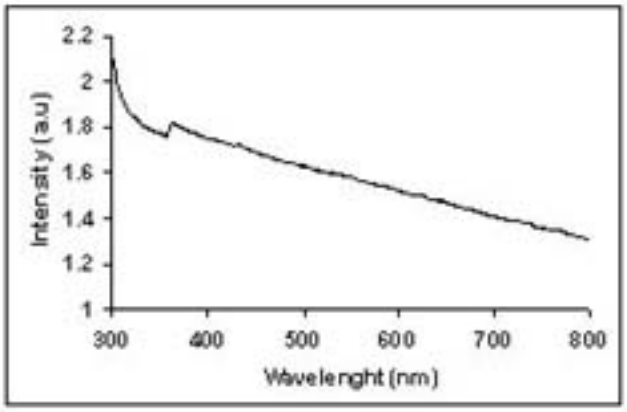

Figure-3(b)
UV_Vis. Spectra of ZnS:Cu

It may be attributed that the small red shift in band edge may be due to the increase in particle size. Stokes shift in nanoaggregates may also play an important role as energy of emission is expected to be higher in small aggregate due to edge effects[13]. The additional peaks at 370nm and 425nm for Cu doped ZnS are also observed which may be attributed to the presence of lattice defects due to sulfur vacancy [2.5.6]. However in the present work the prominence of the peaks indicates some of Cu ions lying in the interstices of host ZnS lattice. It is reported that interstitial Cu ions act as blue centers whereas it act as green centers by host replacing host lattice site of Zn ions. In nanosized ZnS:Cu system, the copper ions form blue centers before green ones and the former can only exist in small

amounts in the samples with lower concentrations which agrees with our doping pattern[14.15]. The absorption intensity increases on copper doping because of the formation of nanosheets.

Conclusion

ZnS and Cu doped ZnS nanoparticles have been synthesized with the particle size of 5 ~ 8 nm which was inferred from XRD and TEM studies. The shape oriented ZnS nanostructures could be successfully prepared by a simple p^H controlled solution synthesized through CBD technique. The XRD patterns show a mixed type structures having crystal planes of both cubic zinc blende and wurtzite hexagonal phases. The XRD patterns also confirm the existence of PVA as capping agent as well as oxide traces in the form of ZnO. TEM morphology exhibits bigger 3D solid triangular shaped particles in undoped ZnS whereas it shows transparent nanosheets on Cu doping. The UV_Visible spectra of ZnS and ZnS:Cu indicate the enhancement of band gap energy due the quantum size effect. It shows a small red shift on copper doping. The results confirm the presence of Cu ions lying in the interstices of host ZnS lattice.

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