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Characterization of Chemically Synthesized Nanofilms

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Abstract: ***In this work, a chemical bath deposition (CBD) method was employed for the synthesis of ZnS nanofilms. These ZnS nanofilms were grown two dimensionally on a silica glass substrate immersed in a colloidal solution of ZnS nanopartilces. These colloidal ZnS nanoparticles were prepared by mixing equivolume and equimolar (0.5M) solution of zinc sulphate dehydrate and thiourea in the presence of ammonia at room temperature and 3% solution of Poly-Vinyl Alcohol (PVA) was added to it as capping agent. In TEM analyses, the formation of the different size of ZnS nanofilms was observed. XRD analysis showed that sample prepared were the cubic Zinc blende structure with particles' size in the ranges 5nm -12nm and the measured spacing of crystallographic plane is about 0.27nm. Room-temperature optical absorption spectroscopy exhibits the presence of two separate excitonic characters inferring that the as-prepared ZnS nanostructures have some crystal defects. Due to the simplicity of this synthesis method, it has a great potential for a rapid and cost-effective preparation of high-quality ZnS nanofilms for use in photovoltaic or photocatalytics applications***

Keywords: CBD, PVA, TEM, HRTEM, etc

1. Introduction

Nanostructure have been a subject of immense interest because of their extensive application such as optical senstiziers, photocatalysis, novel biomolecular application, quantum devices and so on.[1]. Many workers have reported the synthesis of different forms of nanostructures such as nanowires, nanosheets, nanorods nanoplates nanodots, noncombs and nanotubes which have a lot of potential applications in opto-electronics and biosensor nanodevices [2]. Formed nanostruces are sometimes attributed with difficulties to a certain group above because the possibility of formation of nanoforms frequently depends on the synthesis condition. Besides some forms seem similar to each other, so the determination of the final correct form depends much on the audacious imagination of authors [3].

Nanofilms of optically active compound semiconductor are not currently reported as frequently as compared to the other nanostructures such as carbon nanotube [3]. Wide band gap semiconductor containing a great number of defects surface states or doped with optically active luminescence centre have created new opportunities for optical studies and development of application [4]. ZnS is a direct wide bandgap (3.91eV) compound semiconductor with a high index of refraction and a high transmittance in the visible range [5]. Of various types of semiconductor nanostructures, ZnS nanostructures have been extensively studied because of their size or shape dependent electronic and optical properties. [6]. There have been various methods to synthesize nanoscale ZnS particles including single-source molecular precursor, microemulsion, solvothermal route and direct elemental reaction route. In this work we have reported the spontaneous self assemble of PVA stabilized ZnS nanoparticles into uniform and partially transparent nanoflims and their structural and optical properties have been studied.

2. Materials and Method

2.1 Synthesis

The synthesis of ZnS nanoparticles was carried out by a chemical method at room temperature. The principle is the precipitation of the reaction of metal ions and sulfer ions in an aqueous solution. First, zinc sulphate and thiourea were dissolved in deionised water separately. Then equimolar and equivolume of the thiourea solution were mixed together by titration method along with the continuous stirring in the ambient atmosphere [7]. The Poly-Vinyl Alchohol (PVA) was also added to the reaction medium as capping agent. Ammonia solution (1% dissolved in deionised water) was added slowly to metal salt solution to form metal complex and p^H was adjusted between 10 and 12[8]. The milky white precipitated colloidal nanoparticles solution was formed. Finally the clean and dried glass substrate is kept immersed for 24 hours at room temperature to cast the films. The deposited films on glass substrate are dried for characterization

2.2 Characterization

The as-prepared nanofilms of ZnS were taken for XRD study and the colloidal solutions were used for optical as well as TEM studies. The structural investigation of ZnS was carried out using X-ray powder diffractometer (Model: Seifert XSD 3003T/T) with CuK radiation (λ=0.15406 nm) scanning 2θ in the range 20^0- 80^0 . The morphology and electronic diffraction (ED) patterns of the nanoparticles were characterized by transmission electron microscope (TEM) [JEOL 200K] operated at 200CX. Samples were prepared by dispersing a dilute drop of colloids on the copper grid and the excess liquid was removed. Room temperature UV-visible spectra measurement was carried out by UV fluroscent spectrometer [Model:HITACI 113210] in the wavelength range 200nm-800nm. PL spectra are collected between 330nm and 650 nm with excitation wavelength 325nm using

AMINC BOWMAN series-2 luminescence spectrometer [Model:A 357]

3. Experimental Results and Discussion

3.1 Structural Studies

X-ray Diffractogram (XRD) pattern of as-prepared ZnS nanoparticles is shown in the figure-1. It is observed from XRD patterns that ZnS nanofilms are grown. The XRD traces show that ZnS are crystalline with zinc blende type structure. In the figure-1, the three main diffraction peaks correspond to three prominent peaks (200) (220) and (222) at 30.04^0,481.5^0 and 58.7 respectively. It is found that each peak correspond fairly well with data of ZnS in the standard JCPDS no: 80-0020 [7]. From this close agreement it is confirmed that as-prepared ZnS nano-films belong to cubic zinc blende structure. Full width half maximum (FWHM) of XRD pattern peak is broad indicating the formation of the nanocrystal sizes for samples. The average crystal size is determined according to Debye Scherrer's formula using FWHM of the peak presenting the highest intensity and taking into account of broadening [8]. The result confirms the formation of semiconductor nanoparticles with average diameter of 7 nm

The chemical composition and the stichiometry of the ZnS nanofilms were investigated by EDS. The EDX spectra collected from the tip and body part of this nanofilms are displayed in Fig. 2. The presences of Zn and S are clearly revealed in the tip spectra (top) attributing the element purity of ZnS nanofilms [9]. From the bottom spectra corresponding to the nanofilms, the atomic ratio of Zn and S are 51.5 and 48.5 closely matching the chemical stoichimetry of ZnS.

The morphology and dimension of the as-prepared sample were observed by TEM and HRTEM. Fig. 3 (A) shows TEM images of the as-prepared samples indicating the formation of ZnS nanofilms. The product consists of a large number of films like nanostructure with a large lateral dimension of several microns. Many blur-like or ripple type contrast are observed over the ZnS nanofilms. The Fig.3(B) displays SAED patterns of ZnS nanoparticles clearly corresponding to a polycrystalline with some degree of disorder as evident by diffuse rings instead of spots [10] .The particle size measured by TEM is found to be around 6nm[Fig.3(C)]. The high resolution images of as-prepared sample exhibit a fine structure with lattice spacing 2.7nm [Fig.3(D).]

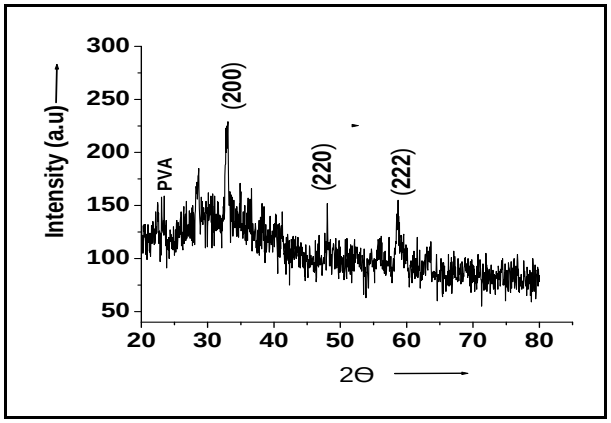

Figure 1: XRD pattern of ZnS Nanofilms

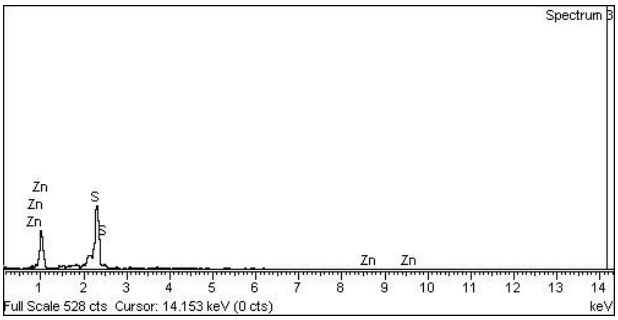

Figure 2: EDS spectra of ZnS Nanofilms

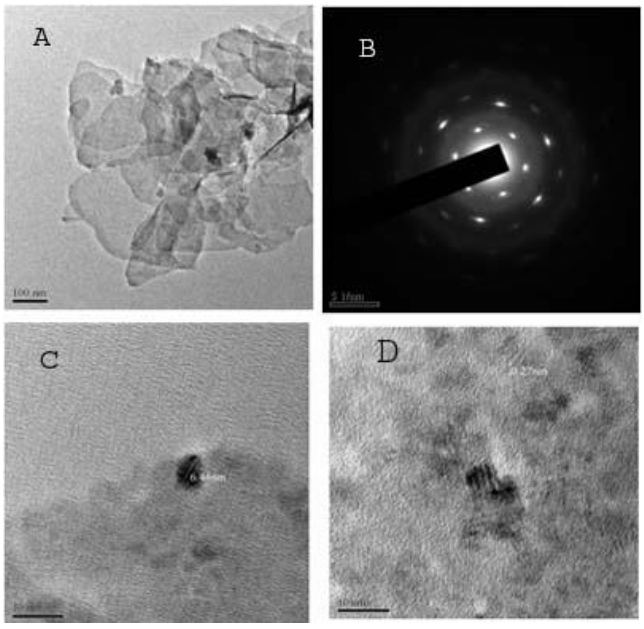

Figure 3: (A) TEM image (B) SAED (C) ZnS Nanoparticles (D) HRTEM of of ZnS;Nanofilms

3.2 Optical Studies

It is well known that optical properties of semiconductor are structure sensitive and they are dependent on the nature and amount of impurities present in the structure [7]. The UV_visible spectra of the aqueous solution containing ZnS nanoparticles are shown in the Fig.4(a). In this figure 4(a)

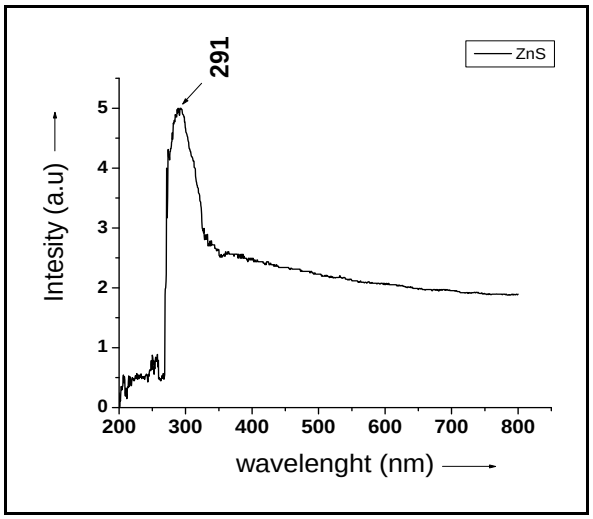

Figure 4(a): UV spectra of ZnS colloidal Nanoparticles

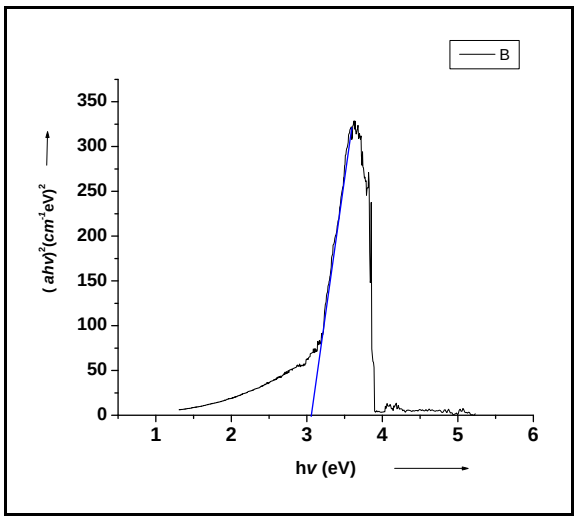

Figure 4(b): Tauc plot of as-prepared ZnS nanoparticles

ZnS nanoparticles display the absorption edge in the range of 291 nm which is at shorter wavelength than 345 nm for bulk ZnS [11].This blue shifted absorption edge is due to the quantum confinement of the exciton present in the sample, resulting in more discrete spectrum of the individual nanoparticles [12]. Fig.4 (b) displays Tauc plots for estimation of band gap. Tauc formulated the following equation to determine band gap energy;

$$(\alpha h\nu)^n = B(h\nu - E_g) \quad \text{(i)}$$

Where, α is the absorption co-efficient, hν is the incident photon energy, B is a constant and E_g is the band gap energy of the material. The exponent depends on the type of the transition. Here, n=2 is taken because the transition is direct. The band gap energy is calculated by extraploting the linear portions of $(\alpha h\nu)^2$ vs hν graph on the hν axis to α = 0 [12]. The estimated band gap energy is found to be 305 eV. From the band gap value of nanoparticle and bulk, the large blue shift of the as-prepared sample is estimated.. Further from this estimated value of blue shift , theoretical size of the nanoparticles can be estimated by using Effective Mass Approximation (EMA) method [13]. The formula in EMA

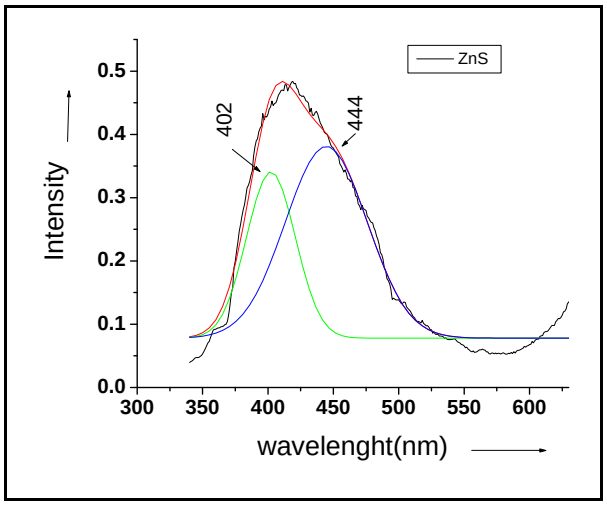

Figure 5: PL spectra of ZnS and deconvoluted spectra of ZnS, red line shows the fitted curve

calculation as derived by I E Brus is given as

$$\Delta E_{gn} = \pi^2 h^2 / 2R^2 / (1/m_e + 1/m_h) - 1.8e^2/\varepsilon R \quad \text{(ii)}$$

Where m_e = effective mass of the electron of the specimen, m_h = effective mass of hole of the specimen, h =6.58 x 10^{-16} eV and R = radius of the nanoparticle. The size of the particle (D) is given by D = 2R and the estimated sizes of ZnS nanoparticle is 7 nm which is quite agreement with TEM measurement.

The room temperature Pl spectra are recorded with 325 excitation wavelength. Figure 3 shows the PL spectra of the ZnS nanoparticles. The deconulated spectra of ZnS show two peaks at 402 and 444nm. Since the sulfer ions are larger than the zinc ions, interstitial sulfer induces more strain to the lattice. Electron levels originating from this site will have smaller binding energies due to such strain [14]. Therefore, interstitial sulfer states should be located closer to the valence band edge. Consequently 402 may be attributed to the interstitial sulfer vacancy while 422nm peaks corresponds to interstitial zinc.

4. Conclusion

Large scale polycrystalline ZnS nanofilms have successfully synthesized through chemical route. The TEM observation confirmed the formation of ZnS nanofilms while XRD results reveal the presence of zinc blende structure of ZnS nanoparticle in the nanofilms. These zinc blende nanoparticles are agglomerated to form polycrystalline as observed in the SAED pattern of the sample. The EDS analysis of the as-prepared sample further indicates the purity of the ZnS. The optical studies reveal the enhanced properties of as-prepared sample as compared to that of bulk ZnS. This study demonstrates that the individual nanoparticles can be used as the fundamental building block for the functionalized, extended nanostructure with enhanced structural and optical properties. This self-assembly method has a promising potential to employ for the synthesis of nanofilms of various technologically important semiconductor nanostructure for their application in futuristic displays, lasser microelectronics and nanosensors.

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References

[1] Shugang Pan, Xiaoheng Liu, "ZnS Graphene nanopartic;Synthesis, Characterization and optical properties",Journal of Solid State Chemistry,191 pp51-59, 2012
[2] C N Rao, et al "Soft chemical approaches to inorganic nanostructures" Pure Appl.Chem., Vol.78(9), pp 1619-1650, 2006
[3] Boris I. Kharisov, "A review for synthesis of Nanoflowers," Recent Patents on Nanotechnology 2008, 2,000-0
[4] Diaz-Reyes, R, Castillo-Ojeda, J. Matinez-Juarez, O. Zaca- Moran, J.E. Flores-Mena and M Galvan-Arellano, "Growth and Characterization of ZnS nanofilms grown by RF magnetron sputtering on GaAs", International Journal of Circuits, systems and signal processing, Volume 8, 2014
[5] Daniel Mooore and Zhong L. Wang, "Growth of anistropic one-dimensional ZnS nanostructure" J.Mater, Chem. 16, pp.3898-3905, 2006
[6] Alvaro A.A.De Queiroz, Mayler Martins, Demetrio AW. Sores, Ecio J Franca, "Modeling of ZnS quantum dots synthesis by DFT technique", Journal of Molecular Structure,873, pp.121-129, 2008
[7] Bodo, Bhaskarjyoti | Kalita, P. K." Chemical Synthesis of ZnS:Cu Nanosheets" ,AIP American Institute of Physics) Conf.Proc- Vol.1276, 31-36 ,2010
[8] Bhaskarjyoti Bodo, Divya Prakash and P K Kalita, "Synthesis and Characterisation of ZnS:Mn Nanoparticles" International Journal of Applied Physics and Mathematics, Vol. 2(2) 181-183, May 2013
[9] Daesoo Kim, Paresh Shimpi and Pu-Xian Gao, "Zigzag Zinc Blende ZnS nanowires: Large Scale Synthesis and Their Structure Evolution Induced by Electron Irradiation, Nanos Res 966-974, 20092
[10] Wenbin Sang, Yongbiao Qian, Jiahua Min, Dongmei Li, Lingling Wang, Wei ,Min Shi, Liu Yinfeng, "Microstructural and Optical properties of ZnS:Cu nanocrystals prepared by an ion complex transformation method" , Solid State Communications, 121 pp.475-478, 2002.
[11] V Ramasamy K Praba and G Murugadoss. "Study of optical and thermal Properties in nickel doped ZnS nanoparticles using surfactants" Superlattics and Microstructures, 51, pp.4403-4409, 2012
[12] Khalid T.Al-Rasoul, Issam m Ibrahim, Iftikhar M Ali, Read M.Al-Haddad, "Synthesis, Structure and Characterisation of ZnS QDs and Unsing it in Photocatalytic Reaction, International Journal of Scientific and Technology Research *vo. 35), 2014*
[13] Bhaskarjyoti Bodo, Nabajyoti Talukdar & P K Kalita, Synthesis of CdS:Cu nanorods for Application In Photonic Devices, International Journal of Engineering Research and Applications *(IJERA)* Vol. 2(4), pp 1656-1659 , 2012
[14] D Denzier, M . Olschewski and K Sattler, "Luminescence studies of localized gap states in colloidal ZnS nanocrytals, Journal of applied Physics, Vol.84 No.5 pp2841- 2845

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