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Synthesis and characterization of CdS nanowires and CdS/TlS nanoflower grown in a polymer matrix by chemical bath deposition (CBD) method

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CdS films and CdS/TlS heterojunction were synthesized on the glass substrate by chemical bath deposition (CBD) within the pores of polyvinyl alcohol (PVA) at room temperature. The bath is made up of solutions of cadmium chloride ($CdCl_2$), ammonia (NH_3), thiourea ($CS(NH_2)_2$), and PVA for fabrication of CdS nanowires. TlS thin films were deposited on glass substrate using a bath that contains thallium nitrate, sodium citrate, sodium hydroxide, thiourea and PVA. For fabrication of CdS/TlS nanoflower CdS thin films were deposited on the TlS thin films. A chemical synthesis process for the fabrication of CdS nanowires and CdS/TlS nanoflower is presented herein. In this present work, these films were annealed in air at 373K and characterized for the structural, morphological, and optical properties. These properties were studied by means of X-ray diffraction (XRD), scanning electron microscopy (SEM), and optical spectrophotometer. The optical properties revealed the presence of direct band gaps with energies 2.20eV for CdS and 1.80eV for CdS/TlS thin films. The films show poor transmittance in the visible and near infrared region of the solar spectrum.

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1. Introduction

One-dimensional nanoscale semiconducting and nanoheterojunction materials have attracted much attention due to their physical properties and potential application in nanodevices [1-3]. The reported nanoheterojuncions includes nanowire/nanowire, nanowire/nanotube and nanotube/nanotube, which show either metal/metal, metal/semiconductor or semiconductor/semiconductor junction behaviour [3]. Nanocrystalline materials have opened a new era in the field of electronic applications and information storage and processing since the nanocrystalline material properties could be altered by changing the crystalline size and/or thickness of the film [4]. Inorganic nanoparticle composites in polymer matrix have been found to enhance optical and electronic properties [5-7]. The deposition of thin films within the self organized pores of polyvinyl alcohol (PVA) via chemical bath deposition is currently achieved by various authors [1, 8-13]. The fabrication of Ag_2S nanoparticles embedded in polymer matrix were synthesized by electrospinning technique [14]. It has been reported that metal chalcogenide nanowires have increased surface area and as such provides better electrical conductivity, when compare with other surface morphologies [2]. These films grown in polymer matrix are basically nanocrystalline in nature.

There are but only few reports on the chemical synthesis (also known as chemical bath deposition, CBD) of nanowires and nanoflowers [15]. Moreover, it requires no sophisticated instruments such as vacuum systems, etc., and the starting chemicals are commonly available and cheap. Also, the preparative parameters are easily controlled. The principles of direct deposition of film via CBD method is based on a gradual release of metal ions from supersaturated solution. A chelating agent is usually used to limit the hydrolysis of the metal ion and impart some stability to the bath, which would otherwise undergo rapid hydrolysis and precipitation.

In this work, we report on the structural, morphology, optical and solid state properties of chemical bath deposited CdS and CdS/TlS thin films in nanowires and nanoflowers form respectively.

2. Materials and methods

2.1 Preparation of CdS nanowire

Glass microscope slides were cleaned by degreasing them in concentrated hydrochloric acid for 24 hours, washed in detergent solution, rinsed in distilled water and dried in oven at 30^{o}C above room temperature. The bath constituents for deposition of cadmium sulphide (CdS) thin films were cadmium chloride ($CdCl_2$) as a source of Cd^{2+}, thiourea [$(NH_2)_2CS$] as a source of sulphide ions (S^{2-}) in the presence of ammonia (NH_3) as the complexing agent. The polyvinyl alcohol (PVA) solution was added to raise the volume of the bath solution. The PVA solution was prepared by dissolving 1.8g of solid polyvinyl alcohol (PVA) in 900ml of distilled water at 90^{o}C. The homogenous solution was aged until the temperature drops to room temperature value. In a typical deposition bath, the solution was composed of 3ml of 1M $CdCl_2$, 5ml of NH_3, 5ml of 1M thiourea and 35ml of PVA solution put in that order. The deposition was allowed to proceed at room

temperature for 90mins after which the coated substrate was removed, washed well with distilled water and allowed to dry. The deposited film was annealed in air at 373K.

2.2 Preparation of CdS/TlS nanoflower

Thin film of TlS was deposited on clean microscope glass slide by using 5ml of 0.2M $TlNO_3$, 4ml of 1M $C_3H_4(OH)(COONa)_3 2H_2O$, 4ml of 1M $(NH_2)_2CS$ and 34ml of PVA solution put in that order in 50ml beaker. The deposition was allowed to proceed at room temperature for 90mins after which the coated substrate was removed, washed well with distilled water and allowed to dry. The glass-TlS system was used as the substrate for the deposition of CdS film. The bath for the chemical deposition of CdS was composed of 3ml of 1M $CdCl_2$, 5ml of NH_3 solution, 10ml of 1M $(NH_2)_2CS$ and 35ml of PVA solution. The deposition time was 360mins. The film was again rinsed thoroughly with distilled water and allowed to dry. The film was also annealed in air at 373K

2.3 Characterization

The deposited films on glass substrate were characterized by using scanning electron microscopy (SEM) JEOL 1600 model. The X-ray diffraction (XRD) analysis was carried out using Rigaku X-ray diffractometer of CuKα wavelength (1.5408Å) (for TlS/CdS thin film). For CdS thin film, the XRD patterns were recorded using X'Pert HighScore PW1710 PANalytical Diffractometer, using the same CuK_α radiation of wavelength λ = 1.5408Å. Optical properties of chemical bath deposited CdS and TlS/CdS thin films were measured at room temperature by using a double beam Perkin-Elmer UV-VIS Lambda 35 spectrometer with glass substrate as a reference in the wavelength range of 300–1100 nm.

3. Results and discussion

3.1 XRD spectra

Fig. 1 (a) shows the XRD patterns of CdS thin films deposited in this work and annealed at 373K. Peak broadening has been observed in recorded diffraction patterns, which shows the formation of crystalline thin films. The most prominent peaks extend from 26.47° and 28.81° in 2θ angular units. The 26.47° peak corresponds to (111) plane which agrees with JCPDS (:#80-0019). The peak at (111) is attributed to cubic CdS having lattice parameters a=b=c= 5.811Å. For the XRD pattern of TlS/CdS thin film displayed in figure 1b, additional peaks have been observed at 2θ angle of 25.58°C and 29.56°C and are identified to be TlS (PDF No 43-1067). These were assigned to the diffraction line produced by (022) and (202) planes [16].

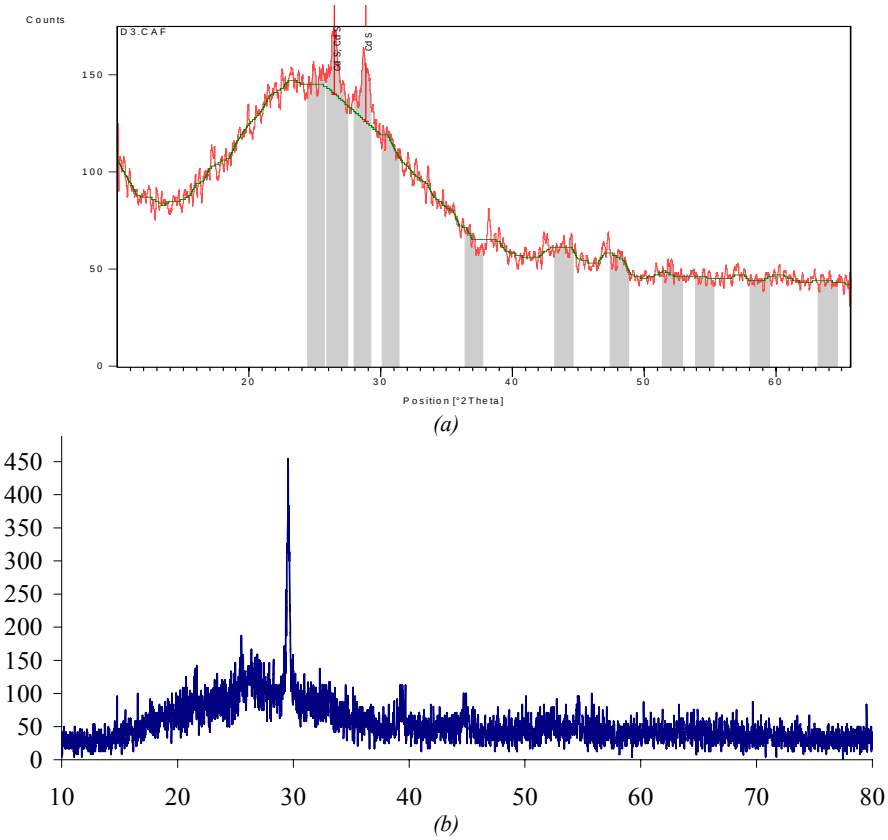
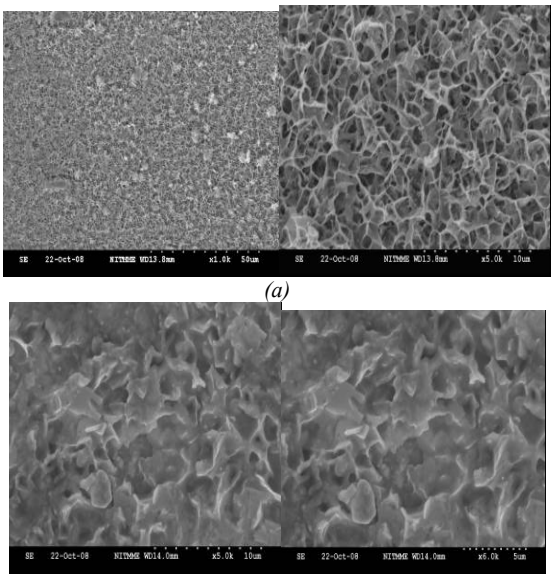


Fig. 1. (a) XRD pattern of CdS thin film; (b) XRD pattern of TlS/CdS thin films.

The average crystallite size of the films was calculated from the recorded XRD patterns using Scherrer formula: $D = 0.89\ \lambda/\beta \cos\theta$, where D is the average crystallite size, λ is the wavelength of the incident X-ray, β is the full width at half maximum of X-ray diffraction and θ is the Bragg's angle. The average crystallite size for the thin film of CdS and TlS-CdS were found to be 16.39nm and 11.30nm respectively.

3.2 SEM

Scanning electron microscopy (SEM) is a convenient method for studying the microstructure of thin films. Figure 2a-b show the surface morphology of CdS and TlS/CdS thin films deposited at room temperature and annealed at 373K at different magnifications. From the micrographs, it is observed that the films are uniform throughout all the regions: the films are without pinhole or cracks



(a)

(b)

Fig. 2. (a). SEM of CdS thin film annealed at 373K at different magnifications; (b) SEM of TlS/CdS film annealed at 373K at different magnifications.

From Fig. 2 (a), we clearly observe the interconnected CdS nanowires. The wires are relatively smooth which is randomly distributed on the glass substrate and their diameters are uniform. Similarly, Fig. 2 (b) shows small nanosized grains engaged in a flower-like structure.

3.3 Optical transmittance and band-gap energy

The variation of transmittance (%T) with wavelength and direct band-gap plot for the two samples under study are shown in Figs. 3 and 4 respectively. A close observation of Fig. 3 shows that the films transmit poorly in the VIS portion of the solar spectrum. In the NIR, CdS has transmittance of between 35% and 50% while that of CdS/TlS is well below 15%. A consequence of the observations is that both films absorb well in the VIS portion of the solar spectrum, as was evidenced in the absorbance-wavelength plot (not shown here). Hence, by forming a heterojunction with TlS, the percentage of solar radiation transmitted by CdS thin film was pulled down by about 35%. In other word, thin film of TlS deposited on CdS increases the absorption of the solar radiation incident on it. The calculated values of the direct energy band gap, from Fig. 4 are 2.2eV and 1.8eV for CdS and TlS/CdS nanocrystalline thin films respectively.

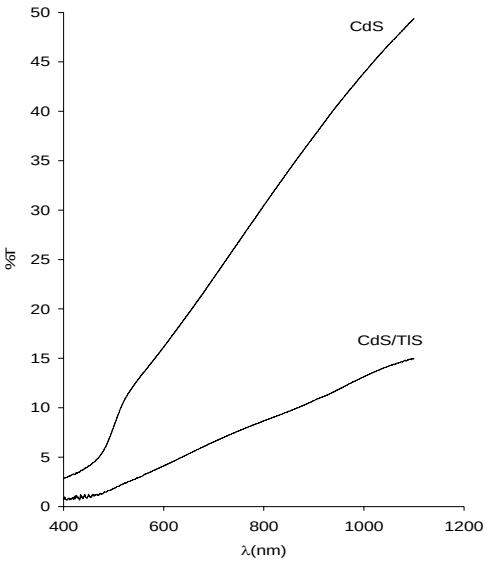


Fig. 3. Plot of Transmittance (%T) vs. wavelength for CdS and TlS/CdS thin films annealed at 373K.

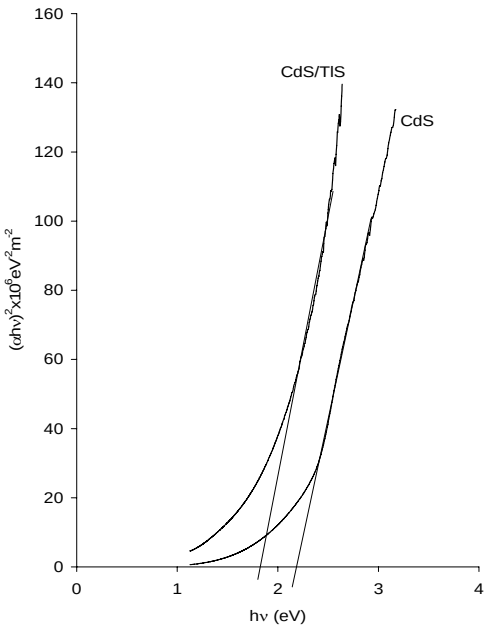


Fig. 4. Plot of $(\alpha h\nu)^2$ vs. photon energy ($h\nu$) for CdS and TlS/CdS thin films annealed at 373K.

A material with a direct band gap lower than 1.9eV and a high absorption coefficient of more than $10^4 cm^{-1}$ has been regarded as a promising absorber for thin film photovoltaic applications **[17]**. The low band gap values exhibited by CdS/TlS thin film together with high absorbance in the VIS make the film ideal for use as absorber material in solar cell application. Hence, by employing CdS as a window material (because of its high band-gap value) and CdS/TlS, as an absorber layer, a simple solar cell based on thin film technology could be fabricated.

4. Conclusions

Nanocrystalline thin films were successfully deposited on glass slide using chemical bath deposition technique. XRD studies reveal that the CdS nanowire have a preferred orientation in the (111) plane of a cubic structure. The average crystallite size was found to be 16.39nmn. For CdS/TlS nanoflower, the diffraction at 2θ angle of 25.58^{o}C and 29.56^{o}C were assigned to the diffraction line produced by (022) and (202) planes. The values of band gap energy exhibited by CdS nanowires are in the required range for the application of the film as window layer in solar cell fabrication. The low band gap energy of CdS/TlS nanoflowers make them ideal for use as absorber material. Duo to their low transmittance in the VIS, the films could also be applied as anti-dazzling coatings in car windscreen and driving mirrors to reduce the dazzling effect of light at night.

References

[1] P. K. Gosh, S. Jana, U. N. Maity, K. K Chattopadhyay, Physica E **35**, 178 (2006).
[2] D. S. Dhawale, A. M. More, S. S. Latthe, K. Y. Rajpure, C. D. Lokhande, Appl. Surf. Sci. **254,** 3269 (2008).
[3] D. Yang, G. Meng, F. Han, L. Zhang, Mat. Lett. **62,** 3213(2008).
[4] R. B. Kale, C. D. Lokhande, Semicond. Sci. Technol. **1,** 20 (2005).
[5] Z. H. Mbele, M. G. Salemane, C. G. C. E. Van Sittert, J. M. Nedeljkovic, V. Djokovic, A. S. Luyt Chem. Mater. **15,** 5019 (2003).
[6] B. O. Dabbousi, M. G. Bawendi, O. Omtduku, M. F. Rubne, Appl. Phys. Lett. **66,** 1316 (1995).
[7] M. Pattabi, B. S. Amma, K. Manzoor, Mater. Res. Bull. **42,** 828 (2007).
[8] P. K. Ghosh, M. K. Mitra, K. K. Chattopadhyay **16,** 107 (2005).
[9] P. K. Ghosh, R. Maity, K. K. Chattopadhyay, J. Nanosci. Nanotechnol. **5**(2), 300 (2005).
[10] S. Jana, R. Thapa, R. Maity, K. K Chattopadhyay, Physica E, 2008, doi:10.1016/j.physe.2008.04.015.
[11] R. Devi, P. Purkayastha, P. K. Kalita, B. K. Sarma, Bull. Mater. Sci. **30**(2), 123(2007).
[12] J. P. Borah, J. Barma, K. C. Sarman, Chalcogen. Lett. **5**(8), 201 (2008).
[13] J. Barma, J. P. Borah, K. C. Sarman, Chalcogen. Lett. **5**(11), 265 (2008).
[14] X. Lu, L. Li, W. Zhang, C. Wang, Nanotechnology **16,** 2233 (2005).
[15] S. D. Chavhan, S. Senthilarasu, L. Soo-Hyoung, Applied Surface Science **254,** 4539(2008).
[16] V. Estrella, M. T. N. Nair, P. K. Nair, Thin Solid Films **414,** 289 (2002).
[17] T. Watanabe, M. Matsui , J. Appl. Phys. **38,** 1379 (1999).

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