

A COMPARATIVE STUDY OF PHYSICAL AND OPTICAL PROPERTIES OF CdZnS AND CdNiS NANOCRYSTALLINE FILMS DEPOSITED BY CHEMICAL BATH METHOD

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In this paper, a comparative study of CdZnS and CdNiS nanocrystalline films deposited by chemical bath deposition (CBD) method has been made using X-ray diffraction (XRD), Scanning electron microscope (SEM), UV-Vis spectroscopy and Photoluminescence analysis. Structure of CdZnS and CdNiS nanocrystalline films were observed by XRD technique was found to be hexagonal. CdZnS nanocrystalline films shows smooth and uniform spherical grains, which are well covered to the substrate, whereas CdNiS film shows nanocrystalline particles spread over the substrate. The crystalline size for CdZnS and CdNiS nanocrystalline films were found to be 17nm and 21nm, respectively. CdZnS films show high absorption than the deposited CdNiS films in the UV range. Photoluminescence spectrum of CdZnS shows more intense green emission than the deposited CdNiS films.

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1. Introduction

In the last few years, considerable interest has been shown in the synthesis of semiconducting nanocrystalline films for optoelectronic applications. Nanostructured materials based on II-VI group compounds have long been known to be suitable materials for photovoltaic device applications because of their high optical absorption coefficients [1-2]. There has been intensified experimental and theoretical research on the effective utilization of the materials in photovoltaic device applications, which requires better controlling of the process parameters[3-4]. Various researchers demonstrated the higher energy bandgap ternary CdZnS has an effective replacement of CdS, because of fewer window absorption losses, and the increase in the short circuit current in the solar cell [5]. CdZnS has a variable bandgap energy of 2.4-3.7eV, is widely used in heterojunction solar cells, high density optical recording, blue and ultra violet laser diodes and in low-voltage cathode luminescence [6]. CdNiS films have low resistivity in light and also have high transmittance in the visible region [7].

The synthesis of ternary metal chalcogenides of group II-VI semiconductors in nanocrystalline form has been a rapidly growing area of research due to their important non-linear optical properties, luminescent properties, quantum confinement effect and other important chemical and physical properties. CdZnS films have been prepared by a variety of techniques like spray pyrolysis [8], dip technique, evaporation, electrodeposition, chemical bath deposition [8], organic chemical vapor deposition [9]. CdNiS films have been prepared by spray pyrolysis and chemical bath deposition method. Of these methods, chemical bath deposition yields uniform, adherent, stable and hard nanocrystalline films with good reproducibility by a relatively simpler deposition method.

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In this paper, we report a comparative study on the structural, surface morphological, optical and photoluminescence properties of chemical bath deposited CdZnS and CdNiS ternary semiconductor nanocrystalline films.

2. Experimental details

In a typical synthesis, the glass substrate was first immersed in concentrated nitric acid for one day, and then washed with deionized water (DI). After that, it was etched with HF (5%) and washed with deionized water, cleaned in acetone, then washed with double distilled water and finally dried in air. The bath constituents for the deposition of CdZnS films were 0.015M cadmium nitrate as a source of Cd^{2+} , 0.015M zinc nitrate as a source of Zn^{2+} , 0.05M thiourea as a source of sulfide ions, S^{2-} in the presence of 0.3M ammonium acetate as the complexing agent. The mixture was stirred well to form a homogenous solution. The cleaned glass substrates were placed vertically inside the beaker for 1hr at 75°C. For the deposition of CdNiS nanocrystalline films, bath constituents for deposition were 0.05M cadmium nitrate as a source of Cd^{2+} , 0.05M nickel acetate as a source of Ni^{2+} , 0.35M thiourea as a source of sulfide ions, S^{2-} in the presence of 0.08M trisodium citrate as the complexing agent. The mixture was stirred well to form a homogenous solution. Then the cleaned glass substrates were placed vertically inside the beaker for 1hr at 75°C. After deposition, the substrates were removed from the bath, rinsed with double distilled water and dried in the air. The films were annealed in the oven at 500°C for 1hr at air atmosphere. To enable optical measurements, the films on one side of the substrates were removed by cotton swabs dipped in diluted HCl.

The crystallographic properties were investigated by using Philips X-ray diffractometer. The morphology of the films was studied using a JOEL SEM scanning electron microscope (SEM) equipment. UV-Vis absorption spectrum was recorded with ocean optics HR4000 high resolution spectrometer. The photoluminescence (PL) spectra of the samples were recorded with a Horiba Jobin Yvon LabRam 800 laser spectrometer.

3. Results and discussion

3.1 X-ray diffraction analysis

X-ray diffraction patterns recorded for the CdZnS nanocrystalline film on glass substrates at bath temperature 75°C, after annealed at 500°C is shown in Fig.1 (a) and for the CdNiS nanocrystalline film on glass substrates at bath temperature 75°C, after annealed at 500°C is shown in Fig.1 (b). The plane exhibited the hexagonal (wurtzite type) structure of CdZnS and CdNiS films. By using the well-known Scherer's relations [12], the crystalline size (D) and strain (ϵ) of the deposited CdZns films were estimated to be 17nm and 0.94, respectively; whereas for CdNiS nanocrystalline films the crystalline size (D) and strain (ϵ) were estimated to be 21nm and 1.48, respectively.

$$D = 0.9\lambda/\beta\cos\Theta \quad \text{and} \quad \epsilon = \beta/4\tan\Theta$$

Where $\lambda=1.5406\text{\AA}$ for $\text{CuK}\alpha$, β is the full width at half maximum (FWHM) of the peak and Θ is the Bragg's angle. The d-values of the lines obtained from the xrd pattern have been compared with the corresponding values for CdZnS and CdNiS films in JCPDS file. The derived d-values are in good agreement with the standard values as shown in table 1 and Table 2.

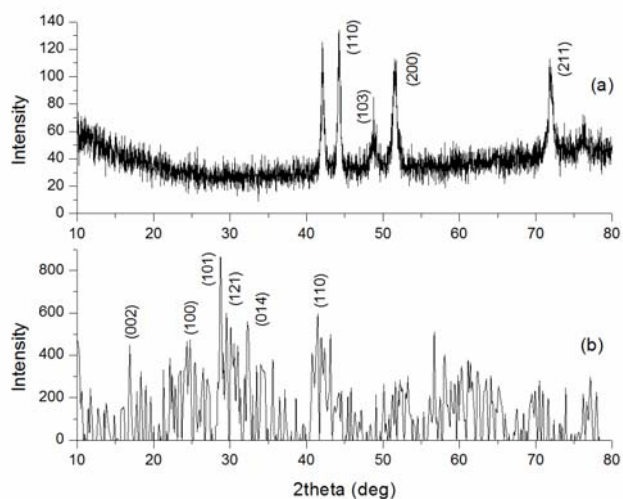


Fig. 1.

Table 1. Comparison of interplanar spacing (d) from XRD and JCPDS data card and corresponding (hkl) planes of CdZnS films

2theta(measured)	d (XRD)	d (ICDD)	(hkl)
44.2	1.91	1.99	(110)
48.82	1.80	1.81	(103)
51.68	1.71	1.72	(200)
72.08	1.21	1.24	(211)

Table 2. Comparison of interplanar spacing (d) from XRD and JCPDS data card and corresponding (hkl) planes of CdNiS films.

2theta(measured)	d (XRD)	d (ICDD)	(hkl)
15.95	5.61	5.67	(002)
24.67	3.56	3.58	(100)
28.75	3.10	3.16	(101)
42.08	2.03	2.06	(110)

3.2 Surface morphology analysis

Fig. 2(a) and 2(b) represents the SEM images of CdZnS and CdNiS nanocrystalline films, respectively. A SEM study shown in Fig. 2(a) reveals the annealing produces the formation of uniformly distributed grains over the entire surface of the substrate. Annealed CdZnS nanocrystalline films shows smooth and uniform spherical grains, which are well covered to the substrate. The CdNiS nanocrystalline film in Fig. 2(b) reveals that the particles are typically spherical in shape with well-defined grain boundaries.

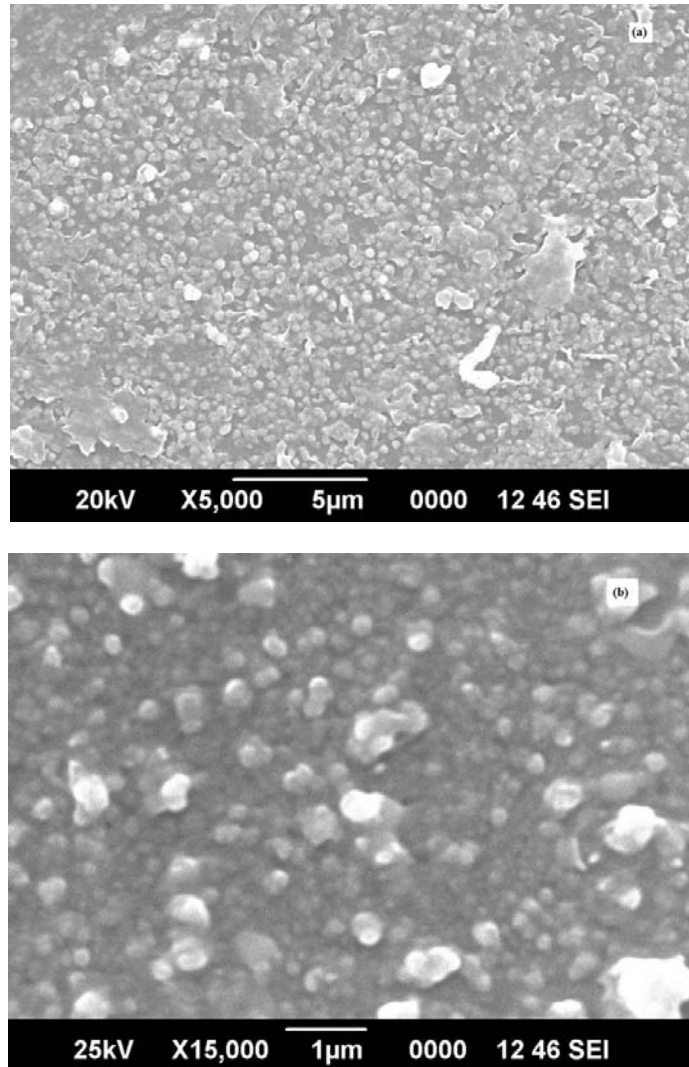


Fig. 2.

3.3 Optical analysis

Fig. 3(a) and 3(b) shows the optical absorption spectra of CdZnS and CdNiS nanocrystalline films, respectively. The optical absorption peak of the CdZnS sample in Fig. 3(a) is around 360nm, whereas for the CdNiS sample in Fig. 3(b), the optical absorption peak is observed at around 380nm. A significant difference in the absorption peak is observed. The higher bandgap of ternary CdZnS has led to less window absorption loss, which makes it an effective replacement for CdS in thinfilm solar cell systems [13].

Fig. 4 shows the transmittance spectra of CdZnS and CdNiS nanocrystalline films. CdZnS (Fig 4a) shows fewer transmittances than CdNiS (Fig 4b) nanocrystalline films [14]. CdZnS films show nearly 45% transmittance in the near UV region, while CdNiS shows 65% transmittance near the UV region [15]. In the visible region, both spectrums show a steady increase in transmittance.

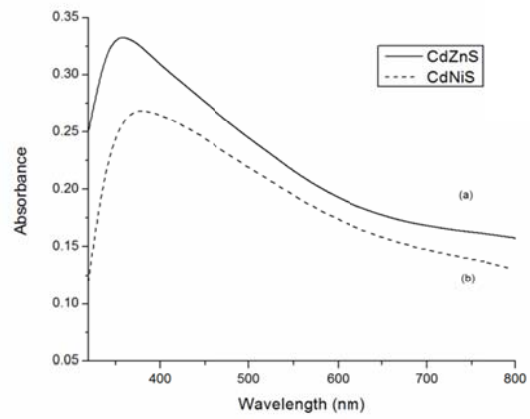


Fig. 3.

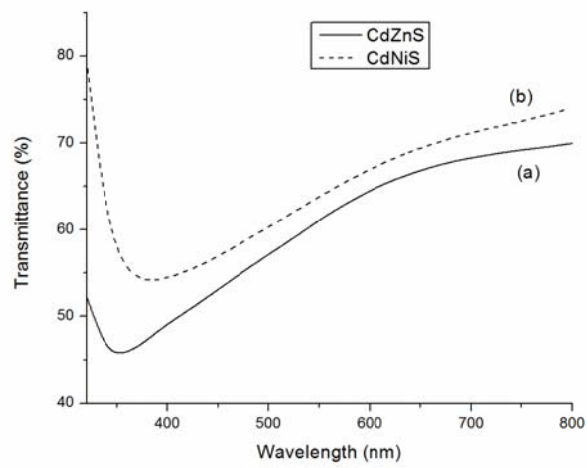


Fig. 4.

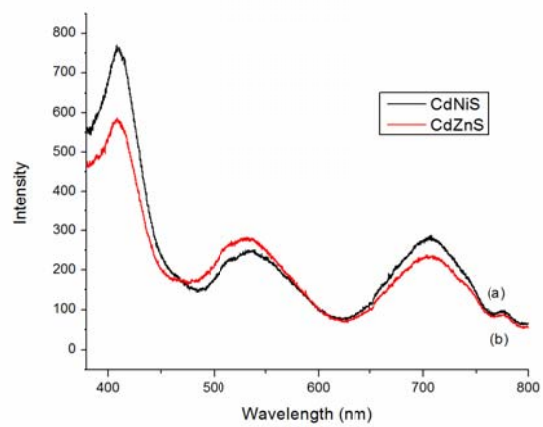


Fig. 5

3.4 Photoluminescence analysis

Fig. 4(a) and Fig. 4(b) shows the photoluminescence spectra of CdZnS and CdNiS nanocrystalline films at room temperature. The PL spectrum of CdZnS in Fig. 4(a) shows two broad diffraction peaks at 540nm and 710nm, whereas the PL spectrum of CdNiS shown in Fig. 4. (b) consist of an intense emission peak at 715nm and a weak broad emission peak at 542nm. For pristine CdS, only a strong peak at 502nm is prominent [15]. The peak at 420nm is due to band edge emission. CdZnS film shows intense green emission due to the presence of Zn content. CdNiS film shows intense red emission at 710nm.

4. Conclusion

In this work we have shown that the CdZnS and CdNiS nanocrystalline films can be chemically deposited on glass substrate at bath temperature 75°C. Crystallography studies, surface morphology, optical and photoluminescence analysis of deposited CdZnS and CdNiS have been investigated. X-ray diffraction technique shows hexagonal structure for CdZnS and CdNiS. CdZnS films show high absorption in the UV range than the deposited CdNiS films. CdZnS films also shows less transmittance than the CdNiS films in the UV range, which makes the CdZnS films are effective replacement for CdS in thin film solar cell system. Photoluminescence spectrum of CdZnS shows more intense green emission than the deposited CdNiS films.

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