Research Article

High-Quality ZnCdS Nanosheets Prepared Using Solvothermal Synthesis

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For the first time, $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ nanosheets with different Zn and Cd ion concentrations were prepared using solvothermal synthesis at 200°C for 4 and 24 h. The crystalline structure of the nanosheets was wurtzite. The optical band gaps of the nanosheets increased with increasing Zn ratio; this increase is consistent with the band gaps estimated using Vegard's formula. The photoluminescence spectra for the 24 h nanosheets had higher emission intensities than those for the 4 h nanosheets. The emission band corresponding to intrinsic near-band-edge emission and a broad peak associated with extrinsic deep-level emission were observed in the photoluminescence spectra.

1. Introduction

One-dimensional (1D) semiconductor nanostructures have recently become widely used because of their special properties: quantum confinement, high surface-to-volume ratio, high optical gain, fast response, and specific crystalline orientation [1–3]. Ternary II–VI semiconductor materials have attracted more interest than binary compounds because some of their properties, such as their tunable optical properties, are better than those of binary compounds. The tunable optical properties of ternary II–VI semiconductor materials can be controlled by appropriately adjusting the constituent mole fractions, particle sizes, and morphologies of the materials [4]. Thus, the formation of $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ led to the control of the optical band gap in a range of ternary phases for CdS (2.42 eV) and ZnS (3.77 eV) [5, 6]. $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ nanocrystalline structures can be obtained using various chemical and physical methods [5, 7–11]. Among the chemical methods, solvothermal synthesis has received considerable attention because of the possibility of preparing high-crystallinity 1D nanostructured materials. Preparation of nanosized metal grids by using lithography led to the fabrication of many types of devices based on

single wires, ribbons, belts, and sheets [12–15]. Single 1D nanostructured devices are more efficient and perform better than optoelectronic and gas sensor devices based on thin films [15]. The solvothermal method can produce high-purity nanocrystalline materials with a high degree of crystallinity compared with other solution-based methods [16]. Herein, the $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ nanosheets were synthesized for the first time via the solvothermal method. The effect that reaction time and Zn ratio had on the morphologies, crystalline structures, and optical properties of the nanosheets was investigated.

2. Experimental Section

Cadmium chloride (CdCl_2), zinc chloride (ZnCl_2), and sulfur (S) powders were used as Cd^{2+} , Zn^{2+} , and S^{2-} ions sources, respectively. The powders were dissolved in 50 mL of ethylenediamine (en) and were stirred for 10 min. The solution was poured into a 100 mL Teflon-lined stainless steel autoclave filled with en to 70% of its total volume. The autoclave was sealed and subsequently loaded into an oven. Four nanocrystalline samples were prepared at 200°C for 4 and 24 h with different ion source concentrations, as

TABLE 1: $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ nanosheets preparation parameters, Zn ratio in the compounds, and optical band gap values.

CdCl_2 concentration (gm)	ZnCl_2 concentration (gm)	Duration time (h)	Zn ratio (%)	Compound	Calculated E_g (eV)	E_g estimated from Vegards' formula (eV)
0.1	0.1	4	0.34	$\text{Zn}_{0.34}\text{Cd}_{0.66}\text{S}$	2.70	2.72
0.03	0.22	4	0.81	$\text{Zn}_{0.81}\text{Cd}_{0.19}\text{S}$	3.42	3.38
0.03	0.12	24	0.7	$\text{Zn}_{0.70}\text{Cd}_{0.30}\text{S}$	3.27	3.20
0.1	0.22	24	0.88	$\text{Zn}_{0.88}\text{Cd}_{0.12}\text{S}$	3.54	3.50

FIGURE 1: FESEM images of ((a) and (b)) 4 h $\text{Zn}_{0.34}\text{Cd}_{0.66}\text{S}$ and $\text{Zn}_{0.81}\text{Cd}_{0.19}\text{S}$ nanosheets, ((c) and (d)) 24 h $\text{Zn}_{0.7}\text{Cd}_{0.3}\text{S}$ and $\text{Zn}_{0.88}\text{Cd}_{0.12}\text{S}$ nanosheets.

summarized in Table 1. After the samples were prepared, the autoclave was removed from the oven and cooled naturally. The resulting precipitates were filtered, washed several times with absolute ethanol and with distilled water, and air-dried at 60°C for 2 h. Field-emission scanning electron microscopy (FE-SEM, FEI Nova NanoSEM 450) was used to determine the morphologies of the products. Quantitative elemental analysis was performed using an energy dispersive spectrometer (EDS) attached to the FE-SEM equipment. The crystalline structure of the prepared ZnCdS nanostructures was investigated using X-ray diffraction (XRD, PANalytical X'Pert PRO MRD PW3040) with $\text{CuK}\alpha$ radiation. Optical absorption and photoluminescence (PL) were measured using a Shimadzu UV-vis spectrophotometer (UV-1800) and Horiba Jobin Yvon H 800 UV equipment.

3. Results and Discussions

Figure 1 shows the FE-SEM images of the samples prepared at 200°C for 4 and 24 h with different Zn and Cd source ion concentrations. The $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ formed nanosheets when the preparation time was 4 h for different ion concentrations. The nanosheet dimensions increased when the preparation time was increased to 24 h, as shown in Figures 1(c) and 1(d), indicating that the sheets grew in length, width, and thickness. Nanoparticles and nanorods were also formed in the 24 h samples. In solvothermal synthesis, solvent type plays an important role in the formation of nanocrystalline materials, especially in determining their structural type. One of the most commonly used solvents to produce nanocrystalline structures is ethylenediamine en ($\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$)

FIGURE 2: EDS spectra of ((a) and (b)): 4 h $\text{Zn}_{0.34}\text{Cd}_{0.66}\text{S}$ and $\text{Zn}_{0.81}\text{Cd}_{0.19}\text{S}$ NSHs, ((c) and (d)) 24 h $\text{Zn}_{0.7}\text{Cd}_{0.3}\text{S}$ and $\text{Zn}_{0.88}\text{Cd}_{0.12}\text{S}$ NSHs.

because of its low dielectric constant (13.82 at room temperature) and boiling point (116°C). It simultaneously acts as a solvent and complexing agent. First, cadmium and zinc ions interact with the lone pair electrons of the en nitrogen atoms to form a $[\text{Zn}_x\text{Cd}_{1-x}(\text{en})_2]^{2+}$ complex. Then, the $[\text{Zn}_x\text{Cd}_{1-x}(\text{en})_2]^{2+}$ complex then reacts with sulfur ions, generated slowly in the solution, to form a two-dimensional

(2D) $\text{Zn}_x\text{Cd}_{1-x}\text{S}-0.5\text{en}$ complex, as shown in the following reactions:

FIGURE 3: XRD patterns of ((a) and (b)) 4 h $\text{Zn}_{0.34}\text{Cd}_{0.66}\text{S}$ and $\text{Zn}_{0.81}\text{Cd}_{0.19}\text{S}$ nanosheets, ((c) and (d)) 24 h $\text{Zn}_{0.7}\text{Cd}_{0.3}\text{S}$ and $\text{Zn}_{0.88}\text{Cd}_{0.12}\text{S}$ nanosheets.

This complex has an organic-inorganic lamellar structure with inorganic ZnCdS sheets separated by organic en molecules that serve as bridge ligands between Cd and Zn atoms in the neighboring inorganic layers and prevent the sheets from aggregating and forming the ZnCdS bulk phase [17, 18]. Wang et al. prepared ZnCdS nanowires by using solvothermal synthesis at 180°C for about 17 h, stirring the solution continuously the whole time [4]. The EDS results suggest that the Zn ratio in the $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ nanosheets increased with increasing ZnCl_2 concentration as shown in the EDS spectra in Figure 2 and listed in Table 1. The crystalline structure was analyzed based on the XRD spectra shown in Figure 3. Diffraction peaks corresponding to the (100), (002), (101), (102), and (112) lattice planes of ZnCdS wurtzite were consistent with those found in the standard data (PDF-4, 00-005-7863). Further, two diffraction peaks appeared at 47.1 and 56° in the spectra for the 24 h samples

FIGURE 4: Absorbance of ((a) and (b)) 4 h $\text{Zn}_{0.34}\text{Cd}_{0.66}\text{S}$ and $\text{Zn}_{0.81}\text{Cd}_{0.19}\text{S}$ nanosheets, ((c) and (d)) 24 h $\text{Zn}_{0.7}\text{Cd}_{0.3}\text{S}$ and $\text{Zn}_{0.88}\text{Cd}_{0.12}\text{S}$ nanosheets.

and could be associated with the (220) and (311) orientations of the ZnCdS cubic phase (PDF-4, 00-005-3822). Moreover, the 24 h $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ nanosheets were more crystalline than the 4 h ones. The preferred growth orientation of the 4 h $\text{Zn}_{0.34}\text{Cd}_{0.66}\text{S}$ nanosheets was along the (002) direction, which changed to along the (100) direction for the 4 h $\text{Zn}_{0.81}\text{Cd}_{0.19}\text{S}$ nanosheets. The zinc ratio had no effect on the preferred growth orientations, along the (110) direction, of the 24 h $\text{Zn}_{0.7}\text{Cd}_{0.3}\text{S}$ and $\text{Zn}_{0.88}\text{Cd}_{0.12}\text{S}$ nanosheets. The UV-vis absorption spectra for the 4 and 24 h $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ nanosheets with different Zn ratios are shown in Figure 5. The absorption edge originally at 459 nm blue-shifted to 362 nm for the 4 h samples when the Zn ratio increased from 0.34 to 0.81%. The 24 h samples exhibited the same absorption behavior: the absorption edge originally at 379 nm, when the Zn ratio was 0.7%, blue-shifted to 350 nm for the 0.88% Zn nanosheets. The optical band gap of the ternary $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ compound can be estimated using Vegard's formula [19]:

$$E_g(x) = E_g(\text{CdS}) + 0.69x + 0.62x^2. \quad (2)$$

The optical band gaps measured for the prepared $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ nanosheets were consistent with the band gaps estimated using Vegard's formula, as shown in Table 1. Figure 4 shows the room temperature photoluminescence (PL) spectra of the $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ nanosheets prepared using different Zn ratios and reaction times. The spectrum for the 4 h $\text{Zn}_{0.34}\text{Cd}_{0.66}\text{S}$ nanosheets had emission bands at 460 and 565 nm: the former corresponds to the intrinsic near-band-edge (NBE) emission (consistent with the optical band gap at this ratio), and the latter is a broad band possibly associated with extrinsic deep-level emission (DLE) [20]. The spectrum for the 4 h $\text{Zn}_{0.81}\text{Cd}_{0.19}\text{S}$ nanosheets had two bands, one at 420 and another at 530 nm. The spectrum for the 24 h nanosheets had stronger emission peaks than those for the

FIGURE 5: PL spectra of ((a) and (b)) 4 h $\text{Zn}_{0.34}\text{Cd}_{0.66}\text{S}$ and $\text{Zn}_{0.81}\text{Cd}_{0.19}\text{S}$ nanosheets, ((c) and (d)) 24 h $\text{Zn}_{0.7}\text{Cd}_{0.3}\text{S}$ and $\text{Zn}_{0.88}\text{Cd}_{0.12}\text{S}$ nanosheets.

4 h nanosheets. The emission spectrum for the $\text{Zn}_{0.7}\text{Cd}_{0.3}\text{S}$ sample had two bands with peaks at 420 and 540 nm, while that for the $\text{Zn}_{0.88}\text{Cd}_{0.12}\text{S}$ nanosheet had bands in the visible region with peaks at 507 and 630 nm as well as small peak located at 344 nm. The broad emission band in visible region may correspond to the surface states of the nanosheet and/or lattice defects, such as vacancies or interstitial sulfur or Zn atoms. The shape and intensity of a band and its location in an emission spectrum depend on defect type concentration [20, 21]. Zhao et al. [11] noted that the PL peak became increasingly blue-shifted with increasing Zn ratio in solvothermally synthesized $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ nanocrystals.

4. Conclusions

$\text{Zn}_x\text{Cd}_{1-x}\text{S}$ nanosheets were prepared using solvothermal synthesis. The nanosheet dimensions increased when the reaction time was increased to 24 h. Analysis of the crystalline structures indicated that the sheets had a hexagonal phase and that crystallinity increased as the reaction time was increased from 4 to 24 h. Furthermore, the preferred growth orientation of the nanosheets depended on the Zn ratio and the reaction time. The optical band gap of the $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ increased with increasing Zn ratio. The PL spectra of the prepared nanosheets show that the 24 h nanosheets had higher emission intensities than the 4 h nanosheets. Band emissions related to intrinsic near-band-edge emission and extrinsic deep-level emissions were observed. The locations of the emission bands depended on the Zn ratios and reaction times.

Acknowledgments

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