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Physical Properties of CdS–In_2S_3 Thin Films

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Abstract—The optical, electrical, photoelectric, and luminescent properties of CdS–In_2S_3 films prepared by spray pyrolysis were investigated. The films were found to consist of solid solutions and/or the compound $CdIn_2S_4$.

INTRODUCTION

Owing to their unique physical and physicochemical properties, semiconducting metal sulfides and their solid solutions are of great interest as promising electronic materials. Particular attention has been paid in recent years to thin films prepared by various techniques. Spray pyrolysis of aqueous solutions of thiourea complexes is a promising technique for preparing films of mixed sulfides. Earlier, we studied the growth and properties of cadmium and indium sulfides. In this work, we focus on the optical, electrical, photoelectric, and luminescent properties of CdS–In_2S_3 thin films prepared by spray pyrolysis and analyze the effect of composition on the properties of the films. According to phase-diagram studies on bulk samples, the CdS–In_2S_3 system contains the $CdIn_2S_4$ compound; In_2S_3 and $CdIn_2S_4$ form a continuous series of solid solutions. The solubility of In_2S_3 in CdS is negligible.

EXPERIMENTAL

CdS–In_2S_3 films were prepared by 600-K spray pyrolysis of aqueous solutions. The starting reagents were analytical-grade $CdCl_2 \cdot 2.5H_2O$, pure-grade $InCl_3 \cdot 3H_2O$, and extra-pure-grade N_2H_4CS. Glass, glass-ceramic, and quartz plates were used as substrates. All films were deposited under the same conditions, by spraying 100 ml of the appropriate solution at a rate of 15 ml/min. The distance between the nozzle and the heated substrate was 40 cm. This procedure made it possible to prepare layers close in CdS : In_2S_3 ratio to the precursor solution, in line with our previous data for other systems [1, 2].

Room-temperature electrical conductivity σ of the films was measured with a dc bridge and a U5-6 amplifier with an input resistance of 10^5 to 10^{12} Ω. A DKSSh-1000 xenon lamp, providing a continuous spectrum in the range studied, was used as an excitation source in photoelectric measurements. Photoluminescence (PL) was excited with a DRSh-100-2 mercury lamp (λ = 365 nm) and measured with an automated spectrometer. Transmission spectra were measured with a VSU-2P spectrophotometer. The optical band gap ΔE_{opt} was evaluated from the position of the intrinsic edge. The phase composition and crystal structure of the films were determined by x-ray diffraction using a DRON-3 powder diffractometer (CuK_α radiation). Density ρ of the films was determined by the immersion technique described in [3].

RESULTS AND DISCUSSION

X-ray diffraction data indicate that some of the CdS–In_2S_3 films contain $CdIn_2S_4$ with the spinel structure (Table 1). The In_2S_3-based solid solution extends to 45 mol % CdS, while the solubility limit of In_2S_3 in CdS is only 2 mol %.

Figure 1 shows the composition dependences of σ and ρ. The weak maximum in σ near 50 mol % In_2S_3 is

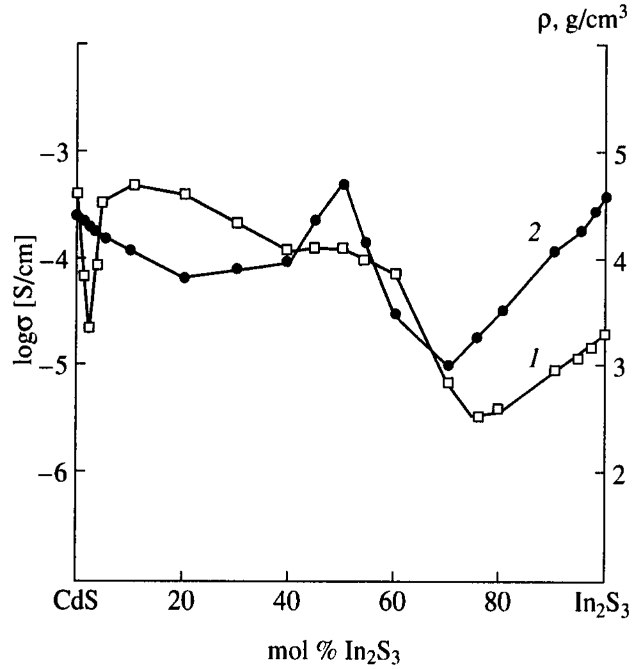

Fig. 1. Composition dependences of (*1*) electrical conductivity and (2) density for CdS–In_2S_3 films.

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Table 1. X-ray diffraction data for CdS–In_2S_3 films

d, nm	*I*, %	*d*, nm	*I*, %	*d*, nm	*I*, %	*d*, nm	*I*, %	*d*, nm	*I*, %	*hkl* [4]	*d*, nm	*I*, %	*d*, nm	*I*, %	*d*, nm	*I*, %	*d*, nm	*I*, %
In_2S_3		85 mol % In_2S_3		75 mol % In_2S_3		55 mol % In_2S_3		50 mol % In_2S_3			35 mol % In_2S_3		5 mol % In_2S_3		2 mol % In_2S_3		CdS	
0.3708	15	0.3754	17	0.3785	13	0.3790	25	0.3790	39	220	0.3790	39	–	–	–	–	–	–
–	–	–	–	–	–	–	–	0.3530	23	–	0.3530	50	0.3583	27	0.3581	25	0.3583	23
0.3203	25	0.3221	78	0.3243	100	0.3220	100	0.3220	65	311	–	–	0.3345	35	0.3342	30	0.3345	25
–	–	–	–	–	–	0.3110	17	0.3110	15	222	0.3220	47	–	–	–	–	–	–
0.2675	100	0.2682	100	0.2698	67	0.2690	31	0.2690	22	400	0.3110	23	0.3148	100	0.3144	100	0.3148	81
–	–	–	–	–	–	0.2200	14	0.2200	13	422	0.2690	10	–	–	–	–	–	–
0.2050	21	0.2053	44	0.2080	47	0.2070	43	0.2070	42	511	–	–	0.2446	16	0.2445	24	0.2446	29
0.1885	20	0.1891	39	0.1900	51	0.1900	68	0.1900	100	440	0.2200	7	–	–	–	–	–	–
0.1340	16	0.1342	18	0.1347	16	–	–	–	–	–	0.2070	89	0.2065	37	0.2064	25	0.2065	24
											0.1960	100	0.1895	13	0.1894	13	0.1895	14
											–	–	0.1760	52	0.1758	61	0.1760	100

likely due to the formation of $CdIn_2S_4$, and the presence of two minima is indicative of a decrease in carrier mobility due to increased scattering, which is probably caused by lattice distortions. The minima in the composition dependence of density support this assumption. We believe that the following factors are responsible for the structural imperfection of CdS–In_2S_3 films:

(1) dissimilar structure types of CdS and In_2S_3,

(2) significant difference in chemical nature between the solvent and solute, and

(3) size mismatch between the host and substituent atoms.

Note that the compounds CdS, $CdIn_2S_4$, and In_2S_3, different in structure, have a higher density than their solid solutions (Fig. 1, curve 2). The density of the $CdIn_2S_4$ film agrees well with the values reported for bulk $CdIn_2S_4$ (Table 2). The sharp minimum in σ near CdS is likely due to the presence of oxygen, since even small amounts of oxygen are known to drastically decrease the conductivity of CdS-rich solid solutions [5]. Note that the films studied here were deposited in air, which led not only to oxygen adsorption but also to stress relieving.

The composition dependence of ΔE_{opt} (Fig. 2) also shows nonmonotonic behavior around the equimolar composition, which supports the formation of $CdIn_2S_4$. The linear decrease in ΔE_{opt} in the range from 55 to 100 mol % In_2S_3 is evidence for the formation of a continuous series of solid solutions. The flat maximum in ΔE_{opt} at high CdS contents supports our assumption that the films contain oxygen on sulfur sites. The oxygen impurity increases bond ionicity and, accordingly, ΔE_{opt} [6]. The composition dependence of the peak photoconductivity (PC) energy shows similar behavior on the CdS-rich side. Note that the CdS–In_2S_3 layers prepared by spray pyrolysis show significant photosensitivity. The difference in the band gaps of CdS and In_2S_3 is not very large (ΔE(CdS) = 2.4 eV, ΔE(In_2S_3) = 2.05 eV), which reflects on the PL and PC spectra of the films. As can be seen in Fig. 3, only the PL intensity varies with film composition, whereas the PL peak position remains unchanged. This effect is explainable in terms of electron transitions from the conduction band to impurity levels. Our results demonstrate that, by adjusting the composition of CdS–In_2S_3 films, one can not only obtain a particular emission of desired intensity but also prepare luminescent layers contain-

Table 2. Physical properties of $CdIn_2S_4$ films prepared by spray pyrolysis

Properties	ΔE_{opt}, eV	ρ, g/cm^3	σ, S/cm	Peak photosensitivity energy, eV	Peak PL energy, eV
Experimental data	2.3	4.8	3×10^{-4}	2.32	1.53 1.68
Literature data for bulk $CdIn_2S_4$	2.3	4.9	6×10^{-4}–2×10^{-4}	–	2.12 2.33

ing two types of radiative centers with controlled relative intensities.

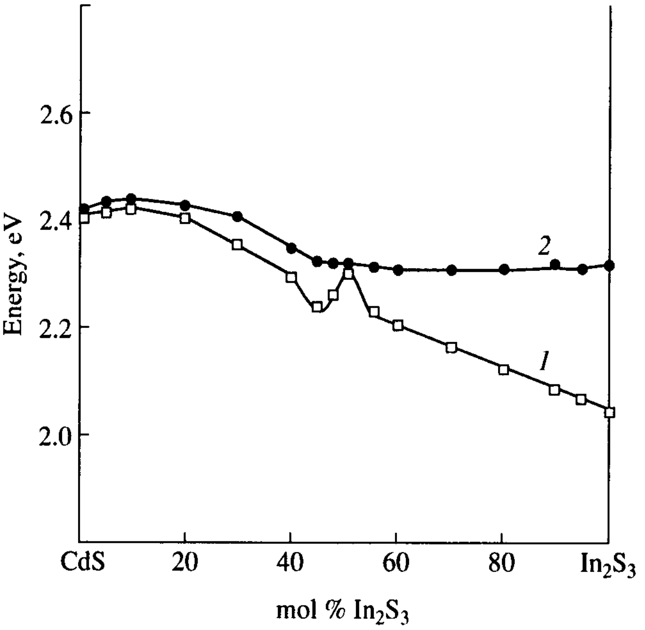

Fig. 2. Composition dependences of the (*1*) optical band gap and (*2*) peak photosensitivity energy for $CdS-In_2S_3$ films.

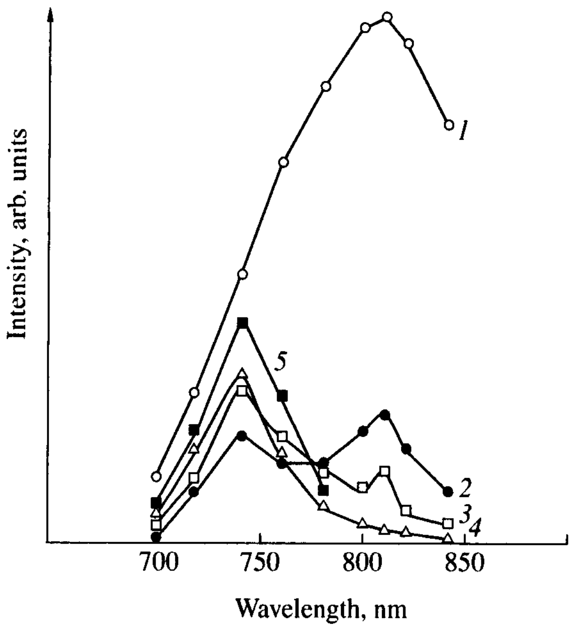

Fig. 3. PL spectra of $CdS-In_2S_3$ films containing (*1*) 0, (*2*) 10, (*3*) 50, (*4*) 90, and (*5*) 100 mol % In_2S_3.

Thus, the $CdS-In_2S_3$ films prepared by spray pyrolysis of aqueous solutions of thiourea complexes exhibit attractive physical properties; the properties of $CdIn_2S_4$ films are identical to those of bulk samples (Table 2).

CONCLUSION

The composition dependences of the interplanar spacings, band gap, electrical conductivity, density, and peak PC and PL energies indicate partial solubility of the constituent sulfides in $CdS-In_2S_3$ films and the formation of $CdIn_2S_4$. The In_2S_3-based solid solution extends to 45 mol % CdS, while the solubility of In_2S_3 in CdS is only 2 mol %. The composition dependences studied show a number of features related to the particular properties and structural perfection of the films.

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