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Energy Procedia 84 (2015) 149 – 155

Energy Procedia

E-MRS Spring Meeting 2015 Symposium C - Advanced inorganic materials and structures for photovoltaics

Crystalline structure, surface morphology and optical properties of nanolamellar composites obtained by intercalation of InSe with Cd

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Abstract

A material composed of InSe and CdSe crystallites was obtained by heat treatment at 753K of InSe single crystalline plates in Cd vapour for 3÷24 hours. The average diameters of CdSe and InSe crystallites determined from diffraction lines analysis are respectively equal to 20 nm and 22 nm. The photoluminescence spectra at 300K and 80K of composite decompose well into two Gaussian curves, one is in good correlation with the photoluminescence of CdSe crystals and the other is shifted to higher energies than the width of the band gap of CdSe crystals.

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Keywords: InSe, Cd, heat treatment, CdSe, crystalline structure, absorption, photoluminescence, crystallites.

1. Introduction

Indium selenide is a semiconductor of lamellar material class with well pronounced structural anisotropy. Such properties like high sensitivity to electromagnetic radiation in the visible and near infrared region, the possibility to

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doi:10.1016/j.egypro.2015.12.308

obtain layers at nano scale thickness by splitting, smooth surfaces at atomic level [1], low density of free valence bonds at surface, are only few factors that determine the perspective of using InSe in optoelectronic and photo-electronic devices as well as in quantum electronics [2-6]. Particularly the InSe material has attractive characteristics for solar energy conversion [7-11]. Having a band gap width of 1.3 eV at room temperature [9, 12] the InSe is ranked as a material with high efficiency for solar cells [13]. However, poly and mono crystalline InSe is also a promising semiconductor for solid electrolyte [14]. Absorption efficiency of photovoltaic and photocathode cells depends of crystal granulation degree [15]. The edge of absorption band for InSe is determined by indirect optical transitions.The energy interval between the edge of indirect and direct absorption band is ~ 50 meV [16]. The absorption coefficient of photons in the region of excitonic continuum is ~10^3 cm^{-1} [17]. This value is lower by more than an order of magnitude than in semiconductors with direct optical transitions like GaAs and CdTe [18,19].The efficiency of light absorption of InSe nano-composites in the near IR region can be increased by adding $A^{II}B^{VI}$ semiconductors.

The InSe single crystals are formed by planar atomic packages that are arranged in Se-In-In-Se structure with ionic-covalent bonds of the atoms inside the packages. The elementary packages are linked by Van der Waals type forces that allow the splitting of plates with smooth surfaces at atomic level and are oriented perpendicularly to C_2 crystallographic axis. The packages are arranged relative to each other in a way that leads to formation of cracks of ~0.3 nm between them [19].

In this paper are examined the crystal structure and optical properties of composite obtained by thermal treatment of InSe lamella in Cd vapor.

2. Experimental details

The InSe single crystals with the concentration of electron of $3 \cdot 10^{13}$ cm^{-3} were grown by Bridgman method from the elementary components of In (5N) and Se (5N) taken in stoichiometric quantities. The plane parallel plates with mirror surfaces were cleaved from crystal ingots. The thickness of plates is 100 ÷ 300 μm. The InSe plates were placed in quartz ampoules with amount of 2 mg/cm^3 of Cd. The vials were evacuated to the pressure of $4 \cdot 10^{-7}$ Pa then they were sealed and heat-treated at the temperature of 753K for 24 hours. After treatment the outer surface and the edges of InSe plates are covered with a granulated layer of reddish colour. A layer of pale-reddish colour is also observed on the surface of cleaved plates.

The crystal structure and surface morphology of InSe plates after heat treatment in Cd vapor were studied by X-ray diffraction ($\lambda_{Cuk\alpha}$=1.54182 Å) using a Shimadzu LabX 6000 diffractometer and AFM microscopy using a NT-MDT SOLVER PRO-M equipment.

The absorption spectra of InSe primary plates have been calculated from transmittance *T* and reflectance *R* measurements at normal incidence using the relation [20]:

$$\alpha = \frac{1}{d} ln \left\{ \frac{(1-R)^2}{2T} + \left[\left(\frac{(1-R)^2}{2T} \right)^2 + R^2 \right]^{1/2} \right\}, \quad (1)$$

where *d* is the sample thickness.

Three InSe plates with thickness of 8.3 μm, 43 μm and 185 μm were taken for absorption measurements.

The PL spectra were recorded using the equipment based on the high optical power monochromator MDR-2 type equipped with two photoreceptors with multi-alkaline and Ag-O-Cs photocathodes. The spectral resolution of device does not exceed 1 meV in analyzed spectral range.

3. Experimental results and discussion

The Fig. 1 shows the AFM surface image of InSe plate subject to heat treatment in Cd vapour at the temperature of 753K (vapour pressure of ~2 kPa [21]). It is known that heat treatment in the range of 470 ÷ 890K in normal atmosphere leads to nano-structuration of InSe plate surface by formation of In_2O_3 clusters and oxides complex of selenium [22,23].

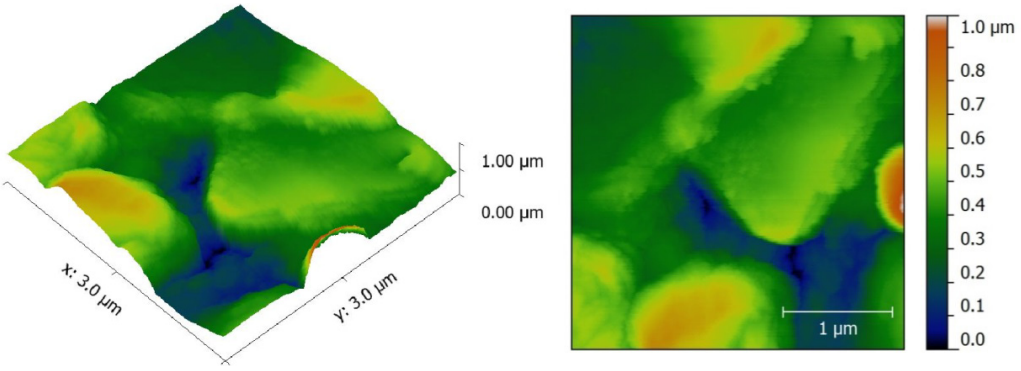


Fig. 1. The AFM image of (0 0 0 1) surface of InSe plate heat treated in Cd vapors at 753K for 3 hours.

The long-term heat treatment of the p-InSe single crystal plates in normal atmosphere leads to coating of surface with a n-In_2O_3 layer which is a good electrical conductor [24]. The plate's surface became micro-structured with poorly defined structure clusters (Fig. 1) by heat treatment of InSe plates in Cd vapor at the temperature of 753K.

The composition and crystalline structure of the obtained material are well observed from the analysis of XRD diagrams (Fig. 2).

The presence of broad band in the range of angles $2\theta = 10°\div15°$ indicates a structure of crystallites with dimensions in the range of micro- and nanometers [25]. The identification of XRD lines using PDF cards is shown in Table 1.

It is easy to observe that the XRD lines from both atomic planes of InSe and CdSe crystallites are present in the Fig. 1 and Table 1. Thus, the composite from CdSe and InSe crystallites is obtained as a result of heat treatment at the temperature of 753K of InSe single crystal plates in Cd vapors. The presence of intense XRD lines at the angles of 24.19°, 25.69°, 42.26°, and 27.31° is an indicator that the final material contains CdSe crystallites with the cubic and hexagonal lattice.

The average size of InSe and CdSe crystallites of composite were determined from the analysis of XRD lines at the angles of 68.21° for InSe crystals and respectively 27.31° for CdSe (Fig. 2, Inset) using the Debye-Scherrer formula [26]. The size of InSe and CdSe crystallites are 22 nm and respectively 20 nm. Thus, it can be admitted that the nanocrystallites of CdSe and InSe are in the composition of the clusters formed on the side surfaces of InSe plates after heat treatment at T = 753K in Cd vapors.

The high perfection of InSe plates used for InSe-CdSe composite is well demonstrated by absorption spectra at the temperature of 300K and 80K in the region of the edge of fundamental band (Fig. 3).

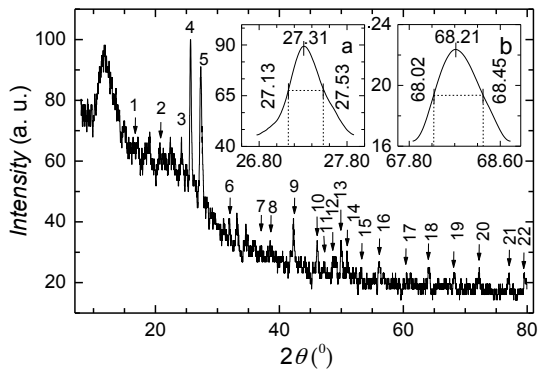


Fig. 2. The XRD pattern of the InSe compound intercalated with Cd at the temperature of 753K. Inset: The contour of diffraction line from: (a) - (1 1 1) planes assembly of CdSe compound; (b) - (8 0 0) planes assembly of InSe compound.

Table 1. The composition of the material obtained by heat treatment of InSe plates in Cd vapor at 753K.

Nr.	Experimental values		ICDD–JCPDS cards				
	2θ,°	I, a. u.	Compound	PDF	2θ,°	I, a. u.	h k l
1	16.37	67.9	InSe	44-1007	16.102	6	0 0 2
2	20.72	66.1	InSe	44-1007	20.523	6	0 1 1
3	24.19	67.9	CdSe	08-0459	23.901	100	1 0 0
4	25.69	100.0	CdSe	19-0191	25.375	100	1 1 1
5	27.31	91.1	CdSe	08-0459	27.080	75	1 1 1
6	31.88	41.1	InSe	80-2272	31.886	25	-4 0 1
7	36.88	32.1	InSe	75-1008	36.867	243	1 0 5
8	38.50	33.9	InSe	71-0354	38.496	621	0 1 8
9	42.26	41.1	CdSe	77-2307	41.999	712	1 1 0
10	46.10	33.9	InSe	34-1431	46.034	28	1 0 7
11	47.30	26.8	InSe	71-0354	47.379	211	0 1 11
12	48.61	28.6	CdSe	65-3415	48.767	111	2 0 0
13	49.92	33.9	CdSe	19-0191	49.740	25	3 1 1
14	50.88	30.4	InSe	80-2272	50.842	166	1 1 2
15	53.16	25.0	InSe	71-0447	53.292	78	2 0 2
16	56.08	26.8	InSe	71-0354	56.071	39	2 0 5
17	60.55	23.2	InSe	80-2272	60.441	14	-2 0 3
18	64.08	25.0	InSe	71-0354	64.101	47	1 1 12
19	68.21	23.2	InSe	80-2272	68.088	54	8 0 0
20	72.26	25.0	CdSe	08-0459	72.292	6	2 1 2
21	77.04	23.2	CdSe	65-2891	77.181	151	4 2 2
22	79.49	23.2	CdSe	08-0459	79.430	18	2 1 3

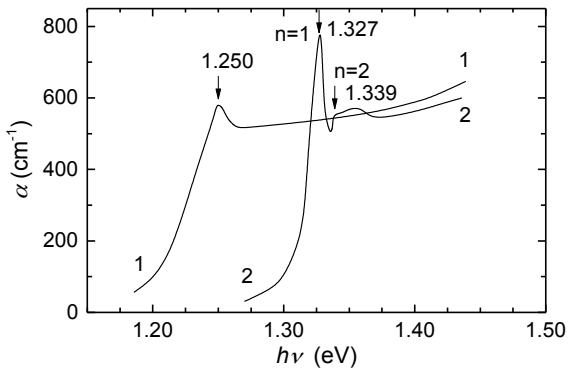


Fig. 3. The absorption spectra of InSe single crystal plate at the temperatures of T = 300K (curve 1) and T = 80K (curve 2).

The peak with maximum at 1.250 eV can be observed at the edge of absorption band at T = 300K. The nature of this peak is highlighted when the temperature decrease to 80K (Fig. 3, curve 2). At this temperature two peaks are present. The first intense one has the maximum at 1.327 eV and respectively the second with low intensity at 1.339 eV. These two absorption lines can be interpreted as the phonon absorption with formation of the direct excitons in n = 1 state ($h\nu_{n=1} = 1.327\ eV$) and the first exciton excited state (n = 2) with the maximum at 1.339 eV [16]. The energy of electron-hole pair binding is equal to 14.6 meV. We would like to mention that direct optical transitions with exciton formation at low temperatures and indirect optical transitions with phonon absorption and emission with 14 meV occurs in InSe crystals [27].

The PL emission spectra excited by He-Ne laser radiation (λ = 632.8 nm) at the temperatures of 300K and 80K for InSe-CdSe composite are shown in Fig. 4. The PL spectra of primary InSe plates at the temperature of T = 80K (curve 1) and of polycrystalline CdSe layer at T = 80K (curve 2) and T = 300K (curve 3) are presented to compare in Fig. 5.

The PL spectra of primary InSe plates contain a structured band with maximum at 1.314 eV and a large threshold with maximum at 1.328 eV (Fig. 5, curve 1). From PL and absorption spectra it can be observed that the particularity localized at 1.328 eV is well correlated with the exciton absorption band in the n = 1 state. The PL threshold at the energies lower than 1.328 eV probably is determined by the luminescent transition valence band – conduction band. The PL emission band with maximum at 1.314 eV can be associated to first phonon repetition of radiative annihilation of free excitons (n = 1 state).

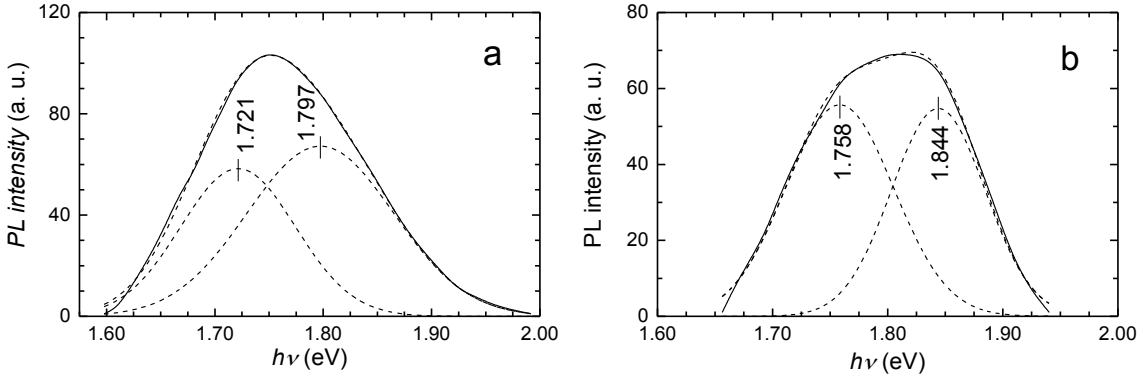


Fig. 4. The PL emission spectra at the temperature of 300K (a) and 80K (b) for InSe-CdSe composite obtained by heat treatment of InSe plates in Cd vapors at the temperature of 753K for 24 hours.

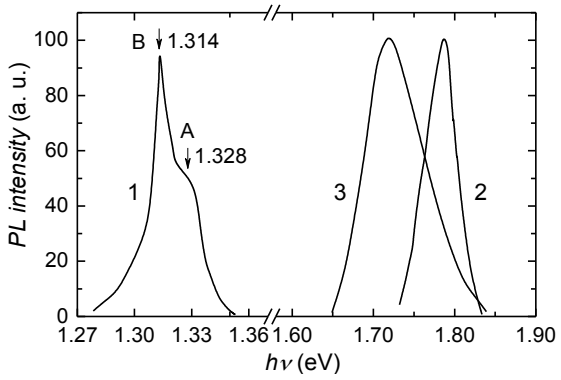


Fig. 5. The PL spectra of the primary InSe plates at T=80K (curve 1) and CdSe polycrystalline layer at T=80K (curve 2) and T=300K (curve 3).

The PL emission spectrum of the CdSe polycrystalline layer at the temperatures of T = 300K and T = 80K is presented through a band with weak asymmetrical contour with maximum at 1.720 eV (T = 300K) and 1.790 eV (T = 80K). It is easy to notice that the PL spectrum at 300K (Fig. 4, a) and 80K (Fig. 4, b) for InSe-CdSe composite is situates in the anti-Stocks region towards InSe PL spectrum, but well correlate's with spectra of CdSe poly-crystals grown as thin layer on glass substrate (Fig. 5).

The wide PL bands of the InSe-CdSe composite at 300K and 80K can be well decomposed in two Gaussian curves with maximum at 1.721 eV and 1.797 eV (300K) and respectively 1.758 eV and 1844 eV (80K). These two PL bands at these temperatures are localized at the energies higher than the band gap for CdSe crystals. However, from the comparison of Fig. 4 and Fig. 5, the PL bands with maximum at 1.797 eV and 1.844 eV are localized at higher energies than those bands in CdSe crystals and in InSe poly-crystals.

As it was established from analysis of XRD lines contour there are InSe and CdSe crystallites with nano dimensions in the synthesized composite. The shape of PL bands and their maximums for sub-micrometer sized crystals depends on the crystallites size. These bands are shifted to higher energies when the size of crystallites decreases [28,29].

The diameter D of the nanoparticles can be determined from the shift of band gap ΔE to higher energies using Brus formula [30]:

$$\Delta E = \frac{\hbar^2 \pi^2}{2D^2}\left[\frac{1}{m_e} + \frac{1}{m_h}\right] - \frac{1.8e^2}{\varepsilon \varepsilon_0 D}, \quad (2)$$

where m_e and m_h are the effective masses of electrons ($0.13\, m_0$) and holes ($0.45\, m_0$) for CdSe [31]; ε - static dielectric permittivity that is equal to 9.6 and ε_0=8.85·10^{-12} F/m.

If we assume that PL band of InSe-CdSe composite (Fig. 4) is composed of PL bands of CdSe micro- crystallites (1.721 eV at 300K and 1.758 eV at 80K) and nano-crystallites (1.797 eV at 300K and 1.844 eV at 80K), the average diameter of CdSe crystallites can be calculated using the equation (2) and it is ~2 ÷ 4 nm. The diameter of CdSe nanoparticles is smaller with an order of magnitude than the size of CdSe clusters (20 nm) that was calculated from the analysis of XRD line contour. The different values of diameter for CdSe clusters calculated using the equation (2) may be caused by the fact that the reduced mass of the electron-hole pair and dielectric permittivity depend on the particle size and the environment [28,32].

4. Conclusions

The InSe and CdSe crystallites composite material was obtained by heat treatment of InSe single crystalline plates in Cd vapor at the temperature of 753K for 24 hours. The composite material has the photoluminescence at the edge of absorption band of CdSe compound.

The average diameter of InSe crystallites from composite was determined from XRD analysis and it is ~ 22 nm.

The diameters of CdSe crystallites from composite are from 2 ÷ 4 nm up to 3÷5 μm.

Acknowledgements

This work was supported by Moldova State University, through the Institutional Grant No. 15.817.02.34A.

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