CRYSTALLINE STRUCTURE AND PHOTOLUMINESCENCE OF GaSe-CdSe NANOCOMPOSITE

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Abstract

A material consisting of CdSe and GaSe crystallites with average dimensions of 34 nm and 30 nm respectively was obtained by heat treatment at 753K and 853K of GaSe single crystal plates in Cd vapors during 24 hours. As a result of Cd atoms interaction with Se atoms CdSe layers are formed both onto outer surface and at interface of layered Se-Ga-Ga-Se packages. CdSe crystallites on the surface grow in the form of plates along C_6 crystallographic axis. Photoluminescence spectra of the composite, at 78K and 300K, contain predominant bands from the luminescent emission of GaSe and CdSe components.

1. Introduction

Layered III−VI compounds represent an emerging class of electronic materials, composed of elementary Chalcogen-Metal-Metal-Chalcogen layered packages. Atomic layers of GaSe consist of 2 monoatomic sheets of Ga sandwiched between 2 monoatomic sheets of Se. The ionic-covalent (predominant) bonding inside a package is much stronger than forces between packages, of Van der Waals type, which determines its specific quasi-*2D* structure and marked anisotropy of physical properties [1].

GaSe single crystal is an optically transparent material in a large wavelength range (0.6−28 μm) [2, 3], exhibits a *p*-type electric conductivity [4] and a band gap of ~ 2.0 eV [5]. These properties along with its high structural anisotropy determine a wide range of applications, including photoelectrical devices [6], linear and nonlinear optics, from electro-optical modulators to THz band generators/receivers [7].

The range of physical properties (suitable for applications) of layered III−VI compounds, in particular of GaSe, can be extended through doping [8] and intercalation [9]. Groups I, II and IV doping elements (Cu, Cd, Zn, Sn) and lanthanide impurities (Gd, Er) [10, 11] lead to an increase in hole concentration from 10^{14} cm^{-3} to 10^{17} cm^{-3} [12, 13].

The characteristic feature of III−VI compounds doping consists of the fact that at low concentrations, impurity atoms liquidate the structural defects present in metal Ga, In) sublattice, while for higher doping concentrations, the exceeding impurity atoms localize mainly between *Se* planes of Se-Ga-Ga-Se packages, producing new hydrogen bonds between Se atoms belonging to neighboring packages. Besides traditional doping mechanisms, substitution and interstitial, impurity insertion (atomic and molecular ions) into the interlayer space (intercalation) is typical for the layered III−VI materials. Presence of impurity intercalated atoms may lead to the formation of novel nano-composites with completely different characteristics and perfectly ordered structures that exhibit atomically flat surfaces, with unusual, controllable (anisotropic) physical properties [9, 14].

In present work structural, morphological and photoluminescence (PL) characteristics of the micro-composite obtained by Cd intercalation (from vapor phase) of GaSe single crystals are examined.

2. Experimental procedures

The starting GaSe single crystals have been grown by Bridgman-Stockbarger technique, from their component elements (all of 5N purity) in a three-zone vertical furnace. From GaSe ingots, plan-parallel plates, of thickness between 60 μm and 300 μm have been split along the *cleavage* planes, from which rectangular samples with surface area of 0.5−2 cm^2 have been cut. Hole concentration in *p*-type selected samples was of 2.5×10^{14} cm^{-3}. Single crystal plates were put, together with 2.5 mg/cm^3 Cd (5N) metal, in quartz ampoules which were pumped down to 5×10^{-5} Torr and tight closed, before being placed inside an electric oven with stabilized temperature in the range of 573−873K, for heat treatment. Samples annealing was performed at temperatures from 753K to 830K, for 12 and 24 h.

The chemical composition of the primary samples and of the intercalated materials has been studied by X-ray diffraction (XRD, CuK_α radiation, wavelength $\lambda_{CuK\alpha}$ = 0.154182 nm) with a DRON-4 apparatus, as well as by micro-Raman scattering experiments.

Surface morphology of lamellar samples and the interface between elementary Se-Ga-Ga-Se packages were analyzed by means of Scanning Electron Microscopy (SEM, Quanta 200 system) and Atomic Force Microscopy (AFM, NT-MDT SOLVER PRO-M equipment) techniques. The PL measurements were carried out in the temperature range of 78−300K and PL excitation was performed by using the second harmonic of a *Nd:YAG* laser (λ=532 nm), with a power density up to 0.5 W/cm^2.

3. Experimental results and interpretations

3.1 Chemical composition of the studied samples

The composition of the material obtained by Cd intercalation of GaSe lamellas was analyzed by X-ray diffraction. The XRD pattern of primary GaSe single crystal samples is shown in Fig. 1.

Parameters of the hexagonal lattice of GaSe single crystals, calculated by using 2θ positions of (202) and (0012) XRD lines, were found to be a = 3.756 Å and c = 15.863 Å.

As can be inferred from XRD patterns presented in Fig. 2 and the Table 1, by Cd intercalation of GaSe lamellas at temperature of 753K, a composite consisting of CdSe and GaSe micro-crystals is formed (Figs. 5 and 6). Peak intensity analysis of XRD patterns shows that CdSe phase (microcrystals) is predominant. At the same time one can mention that CdSe crystallites are formed both on the surfaces of GaSe lamellas and at the interfaces between layered packages.

The XRD pattern of the primary GaSe single crystals displays narrow lines, characteristic for the scattering from micro- and macro-crystallites in the whole 2θ measured range, but the XRD reflections of CdSe-GaSe composite exhibit a wider contour, which is characteristic to the crystallites in sub-micrometer and nanometer range sizes. Crystallite mean size (d) was estimated appealing to Debye-Scherrer's formula [15]:

$$d = \frac{0.94\lambda}{B\cos\theta}, \tag{1}$$

where λ is the X-ray wavelength ($\lambda_{CuK\alpha}$ = 1.54182 nm), B - angular full width at half maximum (FWHM) intensity, and θ - Bragg diffraction angle.

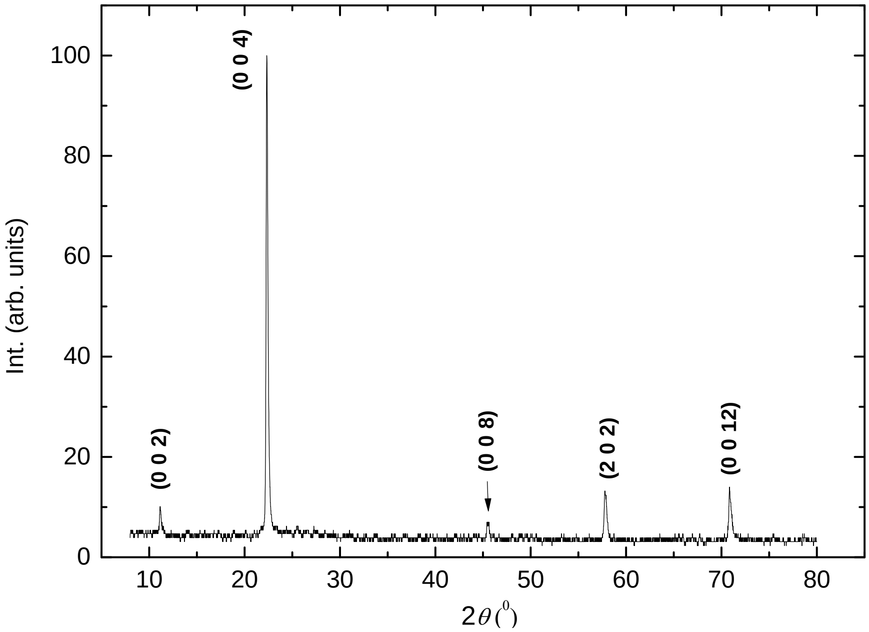

Fig. 1. XRD pattern of GaSe single crystals.

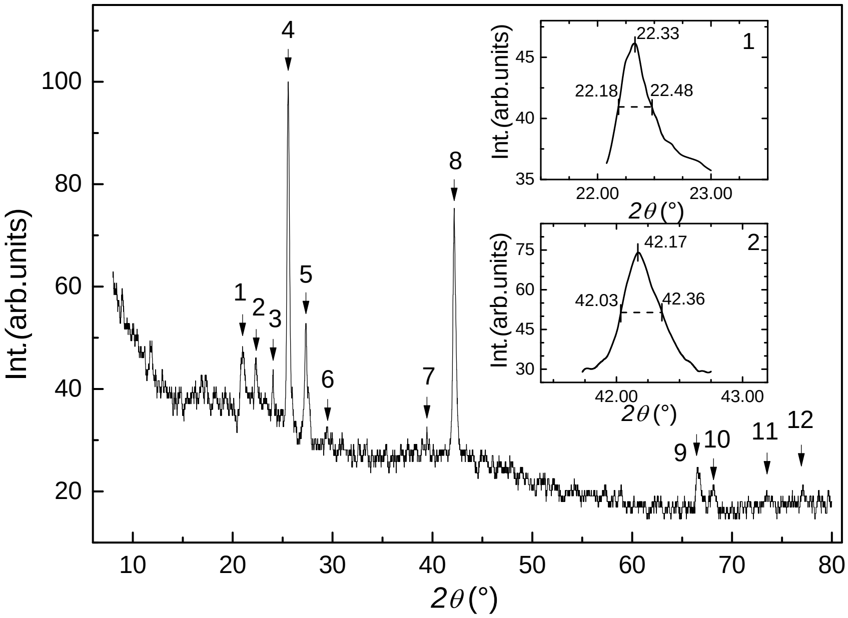

Fig. 2. XRD pattern of GaSe lamella intercalated with Cd at temperature of 753K. Inset 1 – XRD peak profile for the (006) line at $2\theta = 22.33°$ (hexagonal ε-GaSe lattice). Inset 2 - XRD peak profile for the (220) line at $2\theta = 42.17°$ (wurtzite-type CdSe lattice).

Table 1. Structural parameters of GaSe and CdSe components from composite

Nr.	**Experimental values**			**ICDD-JCPDS cards**			
	$2\theta(^{o})$	***Iht-f***	**Sample**	**PDF**	**$2\theta(^{o})$**	***Int-f***	***h k l***
1	20.99	47.44					
2	22.33	45.43	GaSe	81-1971	22.338	99.3	0 0 6
3	24.05	43.8					
4	25.56	100	CdSe	65-2891	25.480	99.9	1 1 1
5	27.33	52.8	GaSe	37-0931	27.623	4	1 0 0
6	29.50	32.24	CdSe	65-2891	29.505	40	2 2 0
7	39.45	32.6	δ-GaSe	29-0628	39.479	20	1 0 10
8	42.17	75.3	CdSe	19-0191	42.044	55	2 2 0
9	66.5	24.7	CdSe	02-0330	66.280	30	2 1 0
10	68.14	21.3	GaSe	79-6611	68.499	1	1 1 16
11	73.5	20.00	CdSe	81-1911	73.511	26	0 0 17
12	76.93	20.00	CdSe	19-0191	76.851	4	4 2 2

Using (006) XRD line located at $2\theta = 22.33°$ (FWHM=5.18×10^{-3} rad) (Fig. 2, Inset 1), of ε-GaSe hexagonal lattice and (220) line at $2\theta = 42.17°$ (FWHM=5.72×10^{-3} rad) (Fig. 2, Inset 2), of CdSe wurtzite-type lattice, average crystallite sizes of ~ 30 nm and ~ 34 nm, respectively, have been found.

3.2 Se-Ga-Ga-Se packages surface and interface morphology

The structural features of layered GaSe compound allow facile crystal cleavage in plan-parallel single crystalline lamellas, atomically smooth and optically homogeneous, of quite different thicknesses, ranging from millimeter down to nanometric size [16]. As was mentioned above, the valence bonds in the outer atomic layer of GaSe lamellas are practically closed, which leads to a low surface state concentration. According to estimates made in [17], the surface state density does not exceed 10^{10} cm^{-2}. Usually, the surface states behave as adsorption centers for ambient atmospheric atoms (molecules), with the formation of Ga and Se oxide nanoislands [18]. SEM images of GaSe surface and of lamellae interface, kept in normal ambient conditions (temperature, humidity, pressure) for over 3 years, are given in Figs.3 and 4, respectively.

If we admit the surface defect based mechanism of nanoislands formation [i.e. formation of the oxide nanoislands (Fig. 3) is mainly due to surface defects of GaSe, which act as adsorption centres for ambient particles], surface state density of cleaved GaSe lamellas can be estimated as $\sim 2\times 10^{10}$ cm^{-2}. One can mention that this value is in good agreement with the estimates made in Ref. [16, 17], which reported surface states densities of ~ 10^{10} cm^{-2} and less.

Therefore, as a result of long time preservation of GaSe plates in normal atmosphere, a nanosized oxide layer (nanoislands), composed of Ga_2O_3, SeO_2, SeO_3, $Ga_2O_3(SeO_4)^{2-}$, $Ga_2(SeO_4)_3$ and gallium selenide hydrate in [19, 20].

At the same time, the interface nanostructuring occurs (Fig. 4), but the size of nanostructuring centers is much smaller in comparison with that for the outer GaSe surface.

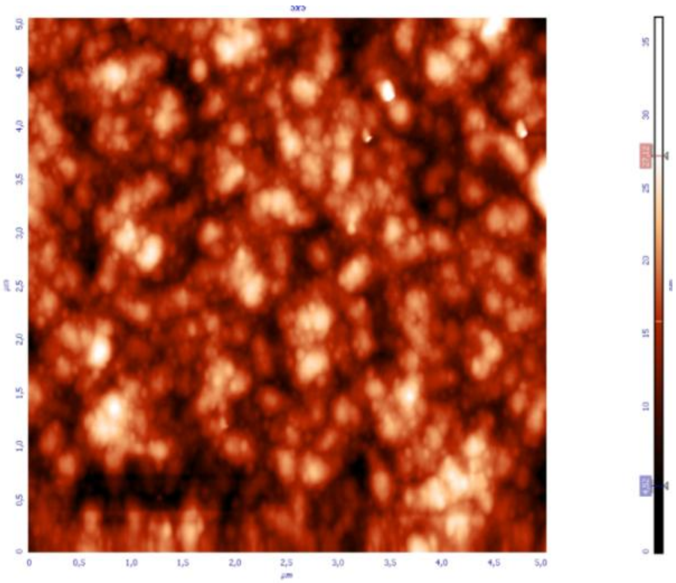

Fig. 3. SEM image of GaSe surface, kept in normal atmosphere.

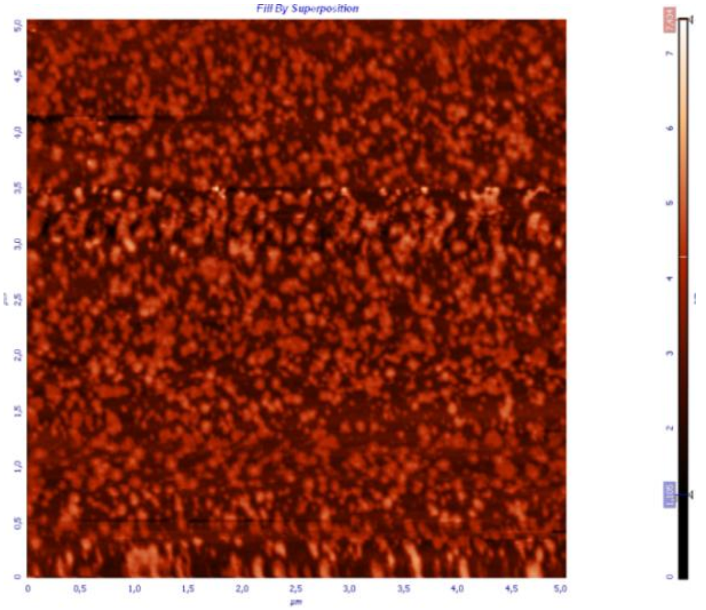

Fig. 4. SEM images of GaSe lamellae interface, kept in normal atmosphere.

In spite the low density of adsorption centers on the surface of GaSe single crystal plates, as a result of Cd-vapor heat treatment at temperatures in the range of 753−833K, formation of variable shape and size microclusters takes place, both on the outer surface and at the interfaces of elementary Se-Ga-Ga-Se packages.

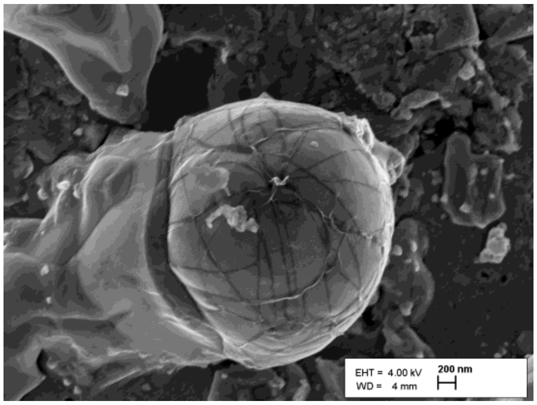

Fig. 5. AFM image of the GaSe plate surface, subjected to a heat treatment at 753K, for 24 hours, in the Cd vapors.

As can be seen in Fig. 5, the microclusters on the GaSe surface grow preponderantly in layers along C_6 crystallographic axis, while at the interface between layered packages flat clusters form (Fig. 6).

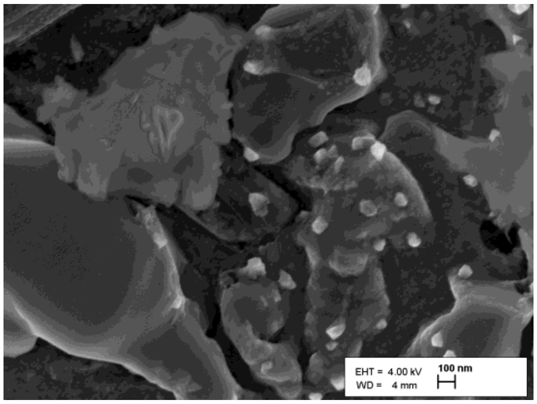

Fig. 6. AFM image of the GaSe plate interface, subjected to heat treatment at 753K, for 24 hours, in Cd vapors.

Nanosized clusters (drops-white spots) can be seen (Fig. 6) on the surface of larger formations, that are produced by Ga metal condensation, which is released from elementary packages as a result of the formation of new compositions (in particular, of CdSe nanoparticles).

3.3 The photoluminescence of non-intercalated and Cd intercalated GaSe lamella

As was demonstrated higher, in the van der Waals crack of GaSe crystal by cadmium intercalation from vapour phase at 833K a composite containing CdSe and GaSe micro- and nano- crystallites is obtained. This material is a radiation source in the red spectrum region when being excited with radiation from absorption band of its components (GaSe and CdSe). At first the PL spectra of GaSe and CdSe in micro- and poly- crystals were analysed.

The PL spectra of CdSe single crystals (Fig. 7), at chamber temperature (a) and at 80K (b), represent *a* band with asymmetric contour and maxima at energy 1.720 eV and 1.787 eV respectively. Whereas the CdSe bandgap at 78K is ~1.84 eV [21] the band with maximum at energy 1.787 eV is associated to free excitons recombination with holes from the acceptor level of energy $E_V + 0.038$ eV.

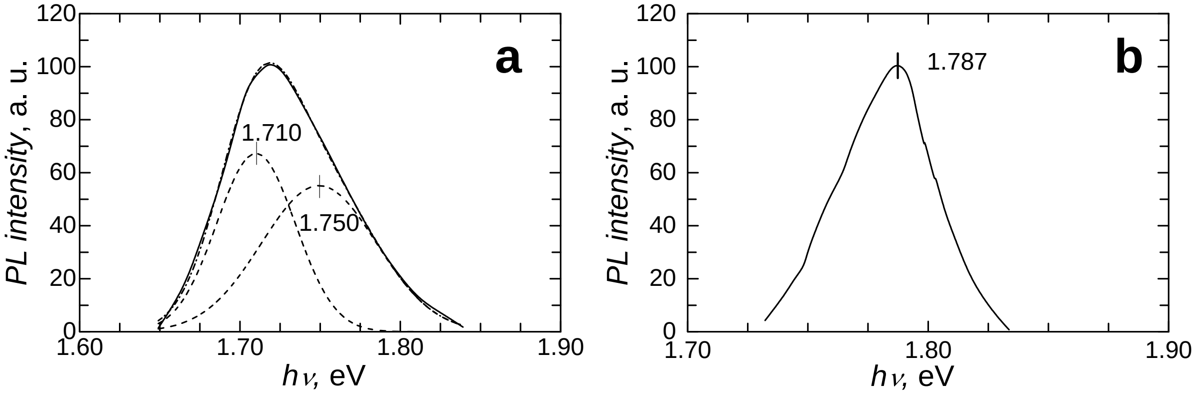

Fig. 7. The PL spectra of CdSe compound at 300K (a) and 80K (b).

The PL spectrum of GaSe single crystals at 80K (Fig. 8), used for GaSe-CdSe composites obtaining, contains at least four bands (A-D) with maxima at energies of 2.091 eV (A), 2.070 eV (B), 2.049 eV (C) and 1.910 eV (D).

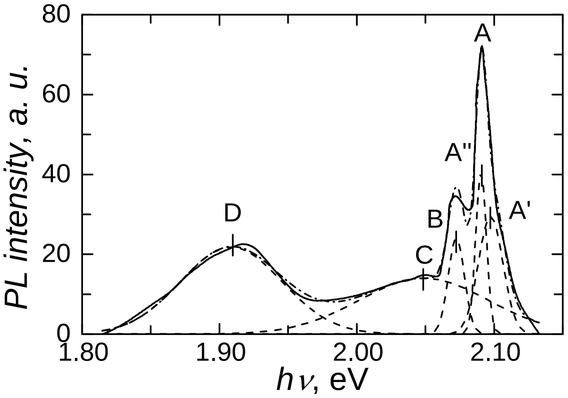

Fig. 8. The PL spectrum of GaSe crystals at 80K.

The band A is well described by two bands with maxima at energies of 2.097 eV (A') and 2.091 eV (A"). The band A' is interpreted as luminescent emission as a result of direct excitons' annihilation [22]. The band A" can be interpreted as radiative emission of excitons localized at neutral acceptor centres with bond energy of ~6 meV [23]. The band B can be considered as first phonon repetition of A" band with phonon emission of energy 19 meV. The band C, with maximum at energy 2.049 eV, well correlates with indirect excitons' energy at 80K and can be considered as luminescent emission of localized indirect excitons [24]. The band D is well studied in [22] where is interpreted as donor-acceptor emission. The own structural defects form in the bandgap of GaSe compound an acceptor level of energy $E_V + 0.152$ eV. The levels of energy $E_C - 0.056$ eV are formed in GaSe by Ga impurities [22] that are present in GaSe as uncontrollable impurities.

The PL spectrum of CdSe-GaSe composite at chamber temperature is composed by a wide band with maximum at energy 1.775 eV (Fig. 9). This band contour can be well decomposed in three Gauss curves with maxima at 1.806 eV, 1.750 eV and 1.691 eV. As result of formation of CdSe crystallites free Ga atoms are obtained. At 833K these atoms are doping the both GaSe and CdSe crystallites. The PL band with maximum at 1.750 eV is also present in the PL spectrum of CdSe single crystals (Fig. 7) and could by caused by radiative band-band recombination. The band 1.691 eV is determined most probably by the Ga and Cd impurities present in CdSe crystallites.

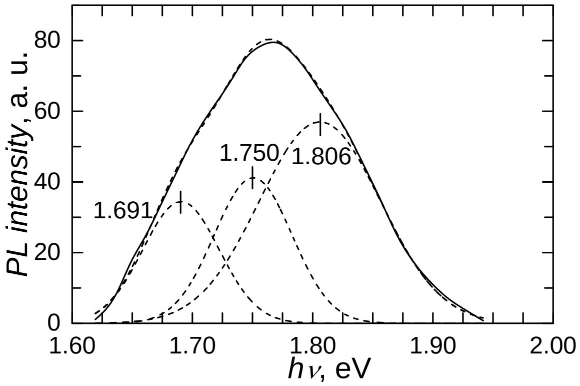

Fig. 9. The PL spectrum, at 300K, of GaSe-CdSe composite obtained by heat treatment of GaSe plates in Cd vapors at 833K for 20 hours.

The temperature decrease from 300K (Fig. 9) to 80K (Fig. 10) leads to PL band increasing in intensity and shifting to higher energies.

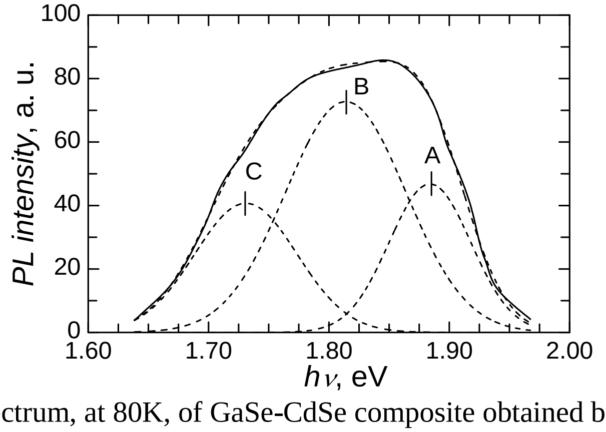

Fig. 10. The PL spectrum, at 80K, of GaSe-CdSe composite obtained by heat treatment of GaSe plates in Cd vapors at 833K for 20 hours.

As we can observe from Fig.10 this band contour decomposes well in three Gauss curves with maxima at energies 1.884 eV (A), 1.814 eV (B) and 1.781 eV (C). As can be observed by comparison of Fig.10 and Fig.8 these three bands are shifted to lowest energies toward PL bands of GaSe compound. So these bands could be associated to luminescent emission in CdSe crystallites from composite. We mention that this band contour is not modified at PL excitation with radiation of He-Ne laser. The energy of this radiation is 1.96 eV and it is lowest than bandgap of GaSe compound which at 80K is equal to 2.104 eV. The bandgap of CdSe crystallites is equal to 1.84 eV [21]. The fundamental absorption edge band of CdSe crystallites at 80K is formed by the band of excitons in the state n = 1 which bond energy is ~16 meV [25]. The band B could be interpreted as radiative emission of localized excitons with the bond energy of electron to ionized donor equal with ~11 meV.

The CdSe layer from the surface has n type conductivity determined by the presence of Se vacancies. The Ga atoms also form a donor level with the energy much smaller than the energy of deep acceptors generated by the Se atoms (energy 0.6 eV [26]). Taking into account these energetic parameters, we can admit that the band C has a donor-acceptor nature with the participation of donors formed by the atoms of Ga impurity, diffused in CdSe crystallites. The band A (1.884 eV) is shifted by ~43 meV inside the absorption band of CdSe compound.

The bands with maxima at 1.806 eV (at T = 300K) and 1.884 eV (at T = 80K) have their maxima localized at energies higher than bandgap of CdSe compound by 66 meV and 44 meV respectively.

It is well known [27; 28] that the PL spectra of CdSe nanoparticles are shifted to higher energies against the PL spectra of single crystals and polycrystalline thin structures. The diameter D of nanoparticles according to the theoretical approach developed by Brus [29] is given by the formula:

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

where m_e and m_h are the effective masses of electrons and holes, which for CdSe are 0.13 m_0 and 0.45 m_0 respectively [30], ε – static dielectric permittivity equal with 9.6, $\varepsilon_0 = 8.85 \cdot 10^{-12} F/m$.

For antiStockes shift of PL band, at T = 300K, equal with ΔE = 66 meV we obtained an average diameter of CdSe nanoparticles of ~0.7 μm. For ΔE = 44 meV, at T = 80K, the average diameter of CdSe nanoparticles is ~0.85 μm. We mention that the average dimensions of crystallites from the sample's outer surface, calculated using formula (1) have the same order of magnitude as dimensions of inhomogeneities presented in the AFM images.

4. Conclusions

- by GaSe lamella intercalation with Cd from vapor phase was obtained the GaSe-CdSe composite consisting of CdSe and GaSe micro-crystallites and condensed CdSe nanoparticles. The defects from the GaSe lamella surface serve as centres of CdSe crystallites formation. These defects' density is about $10^{10}\ cm^{-2}$.
- the CdSe micro-crystallites grow prevalent in the perpendicular direction on to GaSe lamella (0 0 0 1) natural surface.
- the PL spectrum of CdSe-GaSe composite obtained by heat treatment in Cd vapors, at 833K, for 24 hours, at 300K contains the band-band recombination emission bands, since at 80K temperature – annihilation of localized excitons in CdSe crystallites.
- the antiStockes luminescence at 300K and 80K is determined by the reduced dimensionality (~0.8 μm) of crystallites from the composite.

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