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Phys. Status Solidi C, 1–5 (2014) / DOI 10.1002/pssc.201400127

physica status solidi c
www.pss-c.com
current topics in solid state physics

Photoluminescence properties of lamellar nano-composites obtained by Cd intercalation of GaSe and GaSe:Eu single crystals

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Received 29 May 2014, revised 24 September 2014, accepted 24 September 2014
Published online 30 October 2014

Keywords layered semiconductors, composite materials, intercalation, luminescence, rare earths

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In this work surface morphology, composition and photoluminescence at 293 K and 78 K, of composite obtained by intercalation of GaSe and GaSe:Eu (0.49 at.% and 1.00 at.%) single crystal lamellas with Cd from vapor phase at 753 K and 830 K are investigated. As-obtained composite consists of CdSe and microstructured GaSe single crystallites. Photoluminescence spectrum of GaSe:Eu single crystal lamellas is composed of Eu^{3+} emission band ($^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_2$, and $^5D_1 \rightarrow {}^7F_3$ transitions) and indirect exciton line in GaSe crystallites. Emission spectrum of single crystalline GaSe–CdSe composite, at 78 K and 293 K, consists of donor-acceptor band in GaSe microcrystallites and emission band of CdSe crystallites. Composite derived from the intercalation of GaSe:Eu (0.49 at.%) single crystals with Cd exhibits strong visible luminescence. Its quasi-continuous photoluminescence spectrum is produced by superposition of luminescent emissions of CdSe nano- and microparticles, and microstructured GaSe.

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1 Introduction III–VI semiconductor materials (GaSe, GaS, InSe) display a pronounced layered structure, which determines the specific nature of their physical characteristics. Each layer is composed of elementary Chalcogen-Metal-Metal-Chalcogen stratified packages. The links between four monatomic sheets inside a package are accomplished by ionic-covalent (predominant) bonds, while those between packages are comparatively weak forces, of Van der Waals type [1].

Single-crystalline GaSe is known as an emerging material characterized by optical transparency in a wide wavelength range (0.6-28 μm) [2, 3], *p*-type electric conductivity [4] and an energy band gap of ~ 2 eV [5]. Due to its specific features, along with the marked anisotropy of mechanical, electric, optical and photoelectric characteristics, GaSe is a promising candidate for use in photoelectric devices [6] and divers linear and nonlinear optical applications, ranging from electro optical modulators to THz radiation sources/receivers [7].

Application domain of layered III–VI compounds (in particular, GaSe) can be extended through doping [8] and intercalation [9]. Groups I, II and IV elements (Cu, Cd, Zn, Sn) and lanthanide impurities (Gd, Er) [10, 11] determine an increase in hole concentration from 10^{14} cm^{-3} to 10^{17} cm^{-3} [12, 13]. The specific structural features of III–VI materials, in particular formation of a subnanometric gap between neighboring packages, favor intercalation of divers atomic (molecular) ions between chalcogen (S, Se) planes. Impurity atoms, after liquidation of native defects from the metal (Ga, In) sublattice, accumulate at the interface between elementary packages, thus forming new chemical bonds with chalcogen planes. This allows formation of novel nanosized 2D composites with controllable anisotropic physical properties [9, 14].

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In present work morphological, structural and photoluminescence (PL) characteristics of the microcomposite obtained by Cd intercalation (from vapor phase) of GaSe and GaSe:Eu single crystals are studied.

2 Experimental The starting undoped and Eu-doped GaSe single crystal ingots have been grown by Bridgman-Stockbarger technique, from their component elements (all of 5N purity) in a three-zone vertical furnace. Eu doping (concentrations of 0.49 at.% and 1.00 at.%) has been performed during chemical synthesis of GaSe.

From as-grown ingots, optically transparent plan-parallel plates with surface area of 0.5-2 cm^2 have been cut. Single crystal plates with thickness between 15 and 600 μm were put, together with 2.5 mg/cm^3 Cd (5N) metal, in quartz ampoules with internal diameter of 10-12 mm, which were pumped down to 5×10^{-5} Torr and tight closed, before being placed inside an electric oven with stabilized temperature, for heat treatment. Sample annealing was performed at temperatures from 753 K to 830 K, for 12-24 h.

Morphology of the outer surface of lamellas and of the interface between Ga-Se-Se-Ga stratified packages has been examined using Scanning Electron Microscopy (SEM, Quanta 200 system) and Atomic Force Microscopy (AFM, a NT-MDT SOLVER PRO-M equipment) techniques.

Photoluminescence spectra of GaSe based composites have been excited by using monochromatic radiation of a Nd^{3+} (λ=532 nm) laser, with a power density up to 0.5 W/cm^2. Analysis of PL in temperature range of 78-300 K was performed with a photometric equipment including a monochromator with diffraction grating (600 and 1200 mm^{-1}), together with a multi-alkaline photomultiplier. Energy resolution in PL measurements was up to 1 meV over the entire spectral range.

3 Experimental results and discussion Specific features of chemical bonding in GaSe (weak interaction between component stratified packages, in comparison with strong covalent bonding inside them) enable obtaining single crystalline lamellas with atomically flat surfaces [15]. Surface states usually act as adsorption centers for atoms (molecules) from the ambient, with predominant formation of oxide compounds. Figure 1a shows a typical SEM image of the surface of a GaSe lamella, which was preserved under ambient room conditions (temperature, humidity, pressure) for over 3 years. Under the assumption of the surface defect based mechanism of nanoislands formation, surface state density of splitted GaSe lamella can be estimated as ~2×10^{10} cm^{-2}. The obtained value is in good agreement with the estimation performed in Ref. [16], where values of 10^{10} cm^{-2} and below have been reported.

As can be seen from microscopy images (Fig. 1), the outer surface of GaSe lamellas is covered by an island layer of impurity nature. As was stated in Refs. [17, 18], it is composed of Ga_2O_3, SeO_2, SeO_3, $Ga_2O_3(SeO_4)^{2-}$, $Ga_2(SeO_4)_3$ and gallium selenide hydrate islands. These islands may also be found at the interface between Se-Ga-Ga-Se packages. Obviously, surface defects present in GaSe plates behave as condensation centers for Cd onto GaSe surface. Besides, dangling bond defects contribute to the formation of chemical bonds between Cd intercalated atoms and Se atomic sheets from elementary packages. Therefore, as can be inferred from SEM (Fig. 1b) and AFM (Fig. 1,c) images, microsized clusters with irregular shapes do form both on the outer surface of GaSe plates and inside them, at the interface between stratified packages. Surface clusters display a pyramidal growing tendency along C_6 crystallographic axis (Fig. 1c) while those formed at interfaces exhibit a preponderant planar form.

Phase composition of materials obtained by Cd intercalation of GaSe lamellas (both specially undoped and 0.49 at.% Eu-doped) has been analyzed by X-ray diffraction. The XRD diagrams of GaSe lamellas, treated in Cd vapors, at 753 K, for 24 h, contains the next reflexes: (0 0 2), (0 0 4), (0 0 8) and (2 0 2) characteristic for GaSe, and (1 1 1), (2 2 0), (2 1 0) for CdSe respectively, which confirm the GaSe-CdSe composite formation.

In Fig. 2, PL spectra of pure GaSe crystals (curve 1) and Cd-intercalated samples from vapor phase (heat treatment for 20 h, at 830 K), at temperatures 78 K (curve 2) and 300 K (curve 3) are presented. The PL spectrum of undoped GaSe single crystals (Fig. 2, curve 1), at temperature 78 K, is composed of 2 dominant bands (A and B) and a low intensity band, C, with maximum at ~ 2.052 eV.

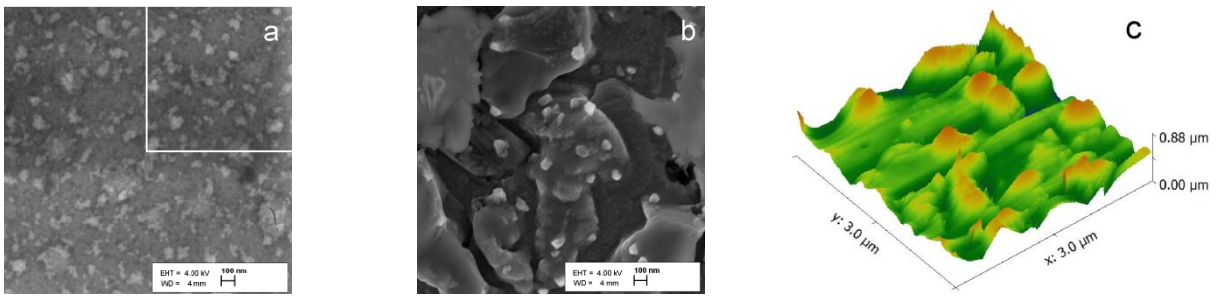


Figure 1 SEM micrographs for the surface of lamella, split from GaSe plate kept under ambient room conditions (a) and interface between elementary packages of the lamella, split from Cd-intercalated GaSe plate at 753 K, for 24 h (b); AFM image of the surface of GaSe lamella, heat-treated in Cd vapors at 830 K, for 24 h (c).

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The band A consists of 2 subbands: a_1, with maximum at 2.092 eV and a_2, peaked at 2.072 eV. The structure of PL spectrum of GaSe single crystals in the region of the fundamental absorption edge is studied in detail in Ref. [19]. Subband a_1 is assigned to radiative annihilation of n=1 free excitons, while a_2, shifted by 20 meV towards low-energy region, is interpreted as bound exciton emission.

Band B, with maximum at $h\nu$=1.92 eV, is produced by donor-acceptor recombination and is present in PL spectra of both undoped GaSe single crystals and doped samples with different elements [20, 21].

By 10−12 h heat treatment in vacuum, at temperature 753-853 K, intensity of band B is decreased down to the background level. Absence of free and localized exciton emission bands indicates that by intercalation, structural defects are formed in GaSe samples, that produce shielding of exciton bonds and lead to quenching of exciton PL.

PL spectrum of CdSe−GaSe composite (obtained by Cd intercalation at 830 K) displays several particularities, among which the absolute maximum (D) at $h\nu$=1.864 eV and plateau E, at $h\nu$=1.790 eV. Particularity D is caused by structural defects created in GaSe lattice of the composite, while energy of plateau E is in good accordance with PL intensity maximum of undoped CdSe crystals, at 78 K. Increasing composite temperature from 78 K to 300 K leads to a decreased (about 30 times) and red-shifted emission band. We mention that threshold G, with energy of 1.72 eV, coincides with maximum of side PL band of CdSe crystals. PL spectrum of CdSe−GaSe composite, at 78 K, contains, in addition to characteristic bands of GaSe and CdSe crystallites, several impurity bands of GaSe crystallites from the composite. Ga and Cd excess may represent such impurities, engendering recombination levels in the GaSe band gap. They are responsible for displacement of the PL maximum, at 78 K, up to 1.65 eV (Fig. 2, curve 2). As can be inferred from Fig. 2, in PL spectrum of intercalated GaSe samples, at 78 K, along with PL bands of GaSe and CdSe, another emission band by 1.65-1.75 eV is also present. This band is also obtained in Se-deficient [22] and Cd-doped GaSe single crystals. Cadmium doping of GaSe engenders an impurity band, maximum of which displaces from 1.95 eV to 1.62 eV for increased Cd concentrations between 0.01 at.% and 0.1 at.% [21], while 1 at.% Se deficiency produces the impurity band peaked at 1.75 eV [22].

Consequently, it can be admitted that at temperature 830 K, Cd atoms from vapors not only intercalate between stratified packages, but also incorporate inside them, creating deep donor and acceptor impurity levels within GaSe forbidden band. Emission band by 1.75 eV has been studied in detail in Ref. [23] and is considered as donor-acceptor recombination between donor level with energy of 0.175 eV (with respect to the bottom of conduction band, CB) and acceptor level located at 0.152 eV above the top of the valence band (VB).

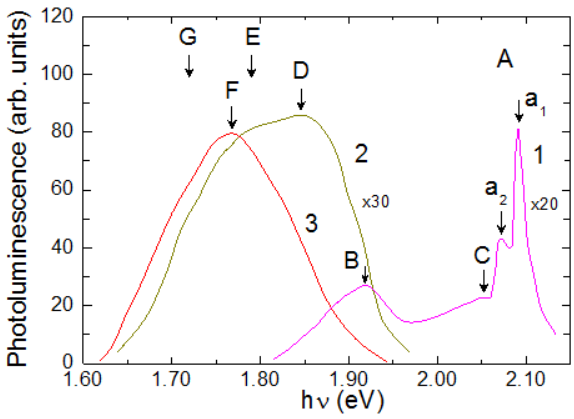


Figure 2 Photoluminescence spectra of GaSe and CdSe single crystals: GaSe-untreated, at T=78 K (curve 1); GaSe-heat treated for 20 h in Cd vapors at temperature 830 K, T=78 K (curve 2) and T=300 K (curve 3). G and E–maxima of the emission peaks of CdSe crystals at temperatures 293 K and 78 K, respectively.

Emission spectra of GaSe single crystals doped with 0.49 at.% (curve 1) and 1.00 at.% Eu (curve 2), at temperature 78K, are illustrated in Fig. 3. Photoluminescence spectra of two samples display similar structures: they are composed of 2 bands (A and B). As can be ascertain from Fig. 3, increasing (by about twice) dopant concentration leads to unequal enhancement of these bands: intensity of PL band A increases more than 2.5 times, while enhancement of the band B is weaker. The PL band A of GaSe:Eu (1.00 at.%), at T=78 K (curve 2), with maximum at 2.16 eV, exhibits a slightly asymmetrical contour in the high-energy region. Two-subband structure is more clearly emphasized in the case of 0.49 at.% Eu-doped GaSe single crystals (curve 1). A complex structure is also exhibited by PL band B, with maximum at ~ 2.04 eV. In order to determine structure of PL spectrum of GaSe:Eu (1.00 at.%), at 78 K, this was decomposed in elementary components. As can be seen in Fig. 3, curve 1, bands A and B can be represented by 2 and 3 (respectively) Gauss curves with maximum at 2.238 eV and 2.158 eV (band A), and 2.052 eV, 2.032 eV and 1.996 eV (band B). A similar structure is registered in the case of higher intensity emission of 1.00 at.% Eu-doped samples. According to energy level diagram for Eu^{3+} [24], PL subband described by curve a_1 is obtained as a result of transition $^5D_1 \rightarrow {}^7F_3$, while subband a_2 is produced by electric dipole transition $^5D_0 \rightarrow {}^7F_1$. Besides, electric dipole transition of Eu^{3+} from $^5D_0$ to $^7F_2$ levels leads to a structure with 2 subbands, b_1 and b_2, peaked at 2.032 eV and 1.996 eV, respectively.

Energy position of subband b_3, equal to 2.052 eV, is in good accordance with that of indirect exciton emission band in GaSe, at temperature 80 K [25].

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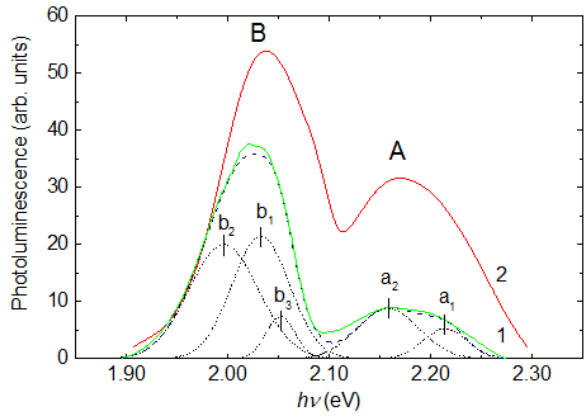


Figure 3 Photoluminescence spectra of GaSe:Eu (0.49 at.%) (curve 1) and GaSe:Eu (1.00 at.%) (curve 2), at T=78 K. Dashed line – convolution of elementary bands.

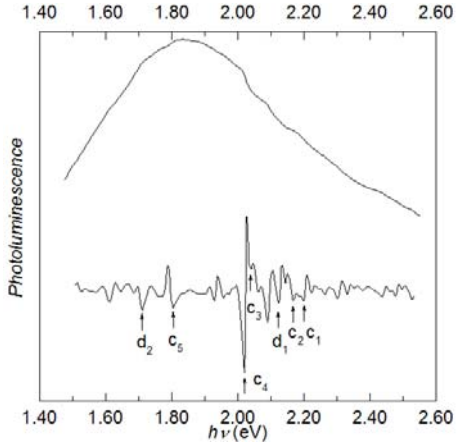


Figure 4 Photoluminescence spectra of GaSe:Eu–CdSe composite at T=78 K.

Photoluminescence spectrum of GaSe:Eu–CdSe composite, at temperature 78 K (Fig. 4), consists of a poorly contoured band covering a wide energy range, from 1.6 eV to ~2.85 eV at T=293 K, and from 1.5 eV up to 2.55 eV, at T=78 K. By comparing PL spectra of GaSe−CdSe (Fig. 2, curve 2) and GaSe:Eu−CdSe (Fig. 4) composites, it can be seen displacement of PL band from 1.5 eV to 2.1 eV, together with its high-energy broadening, up to ~2.9 eV. In order to emphasize main particularities of emission spectrum, in Fig. 4 second derivative PL spectrum, in the energy range 1.5−2.6 eV, was also represented.

Well-pronounced peaks of this spectrum indicate the component PL bands: c_1 (2.200 eV), c_2 (2.167 eV), c_3 (2.040 eV), c_4 (2.021 eV) and c_5 (1.804 eV). Presence of mentioned particularities in PL spectrum of GaSe:Eu−CdSe composite can be explained under the assumption that in light-emitting process, radiative transitions of Eu^{3+} in GaSe crystallites and donor-acceptor transitions in CdSe crystallites take place. The d_1 and d_2, bands energies correspond to band-band emission in GaSe and donor-acceptor emission in CdSe crystallites, respectively.

4 Conclusions By Cd intercalation (from vapor phase) of GaSe lamellas, GaSe−CdSe and GaSe:Eu (0.49 and 1.00 at.%) micro-composites are obtained. Defects present at the lamellar surface (density of about 10^{10} cm^{-2}), as well as at the interface between stratified packages of GaSe single crystals, behave as formation centers of CdSe crystallites.

Photoluminescence spectrum of GaSe−CdSe microcrystalline composite consists of impurity and indirect exciton emission bands in GaSe crystallites, and donor-acceptor PL band peaked at 1.72 eV (T=293 K) and 1.79 eV (T=78 K) in CdSe crystallites.

At 0.49 at.% and 1.00 at.%, dopant concentrations, the europium impurity atoms create Eu^{3+} luminescence centers in GaSe single crystals. Photoluminescence spectrum of GaSe:Eu single crystals is composed of Eu^{3+} PL bands ($^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_2$ and $^5D_1 \rightarrow {}^7F_3$ transitions) and emission band of indirect excitons in GaSe.

GaSe:Eu−CdSe composite exhibits photoluminescence properties in photon energy range 1.5-2.5 eV. Its PL spectrum is composed of Eu^{3+} emission bands in GaSe and those of CdSe crystallites from the composite.

Acknowledgements This work was supported by Moldova State University, through the Institutional Grant No. 11.817.05.12A.

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