PREPARATION AND OPTICAL PROPERTIES OF LAMELLAR GaSe–ZnSe NANOCOMPOSITES

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Abstract

ZnSe–GaSe nanocomposite plates photoluminescent in a photon energy range of 1.80−2.64 eV were obtained via exposing GaSe single-crystal plates to a Zn-vapor heat treatment at temperatures of 673−873 K. The photoluminescence spectrum is dominated by the self-activated emission band of ZnSe with a maximum at 2.04 eV. The average size of the ZnSe crystallites is ~45 nm. The absorption spectrum of the composite consists of two regions characteristic of direct optical transitions in GaSe crystals with a band gap of 1.99 eV and ZnSe crystallites with a band gap of 2.56 eV at room temperature.

1. Introduction

Layered III−VI group semiconductors, in particular of GaSe, have been intensively studied in recent years because of promising application in optoelectronics (visible region), nonlinear optical devices, and radiation generation/detection in THz domain [1−4].

GaSe single crystals are composed of flat Se–Ga–Ga–Se elementary packages perpendicular to its C_6 crystallographic axis [5].

The links between the packages are of Van der Waals type, much weaker than those between four monoatomic sheets inside a package, accomplished by ionic-covalent (predominant) forces. This feature results in a marked anisotropy of mechanical properties (facilitating intercalation) and electric, optical, and photoelectric characteristics.

At the same time, the valence bonds of chalcogen atoms at the interface between stratified packages are almost closed; the relative arrangement of elementary packages provides the formation of a subnanometric (0.3 nm) gap between the neighboring packages favoring the intercalation of diverse atomic (molecular) ions between chalcogen planes [6−8].

GaSe intercalation may lead to new physical properties of the material, such as ferromagnetism and magnetoresistivity.

Owing to compensated valence bonds at the surface of stratified packages, gallium monoselenide intercalated with Li and H also displays marked solid electrolyte properties [9, 10].

The presence of Se atomic planes at the surface of GaSe plates enables obtaining

heterojunctions exhibiting visible photosensitivity by heat treatment under normal atmosphere or metal vapor atmosphere [11].

By metal vapor-heat treatment of layered GaSe single crystals, a metal-chalcogen compound layer is formed at the GaSe surface, together with intercalation of metal atoms between stratified packages to form lamellar nanocomposites.

In this work, the composition and optical properties of the composite obtained by Zn vapor-phase intercalation of GaSe single-crystal plates are studied.

2. Experimental

p-GaSe single crystals, which were used as starting materials, were grown by the Bridgman technique from their component elements (Ga and Se, both of 5N purity) taken in stoichiometric portions.

Hole concentration and mobility at room temperature were about 4×10^{14} cm^{-3} and 35 $cm^2/(V \cdot s)$, respectively.

GaSe plates with a thickness of 100−300 μm obtained by splitting single crystalline ingots along the (0001) atomic planes were used for the preparation of the composite. They exhibited mirror-like surfaces showing no defects visible at 600× magnification.

Selected GaSe single-crystal plates were placed, together with 5% Zn, in quartz ampoules with an internal diameter of 10–12 mm; the ampoules were evacuated to 5×10^{-5} Torr, tightly closed, and placed in an electric oven with stabilized temperature for heat treatment at 833 K for 3−24 h. As a result of the heat treatment, the surface of the GaSe plate was covered by an orange granular layer with a micrometer size. The surfaces of the freshly split plates also exhibited a granular microstructure.

The crystal structure and composition of the as obtained material were analyzed by X-ray diffraction (XRD) technique using a DRON-4 diffractometer (CuK_α radiation, $\lambda = 0.154182$ nm). Measurements were conducted in an angular range of $10° < 2\theta < 80°$ with a peak resolution of 0.05° and 10° min^{-1}scan speed.

Diffuse reflectance spectra were registered using an M-40 spectrophotometer equipped with an integrating sphere. A pressed $BaSO_4$ powder was used as a white reference standard.

Low-temperature photoluminescence (PL) measurements were conducted using a cryostat with quartz windows in a temperature range of 78−300 K. The PL of the GaSe-based samples was excited using a N_2 laser (λ = 337.4 nm) with an average power of 100 mW. The PL spectral characteristics of as obtained samples at 78 K were recorded on a spectrophotometric setup including a monochromator with a diffraction grating (600 and 1200 mm^{-1}) and a photomultiplier with a multi-alkaline Na_2KSb:Cs photocathode. The energy resolution was up to 2 meV over the entire measuring range.

3. Experimental results and interpretation

Fig. 1 shows the X-ray diffraction pattern of the primary GaSe single crystal.

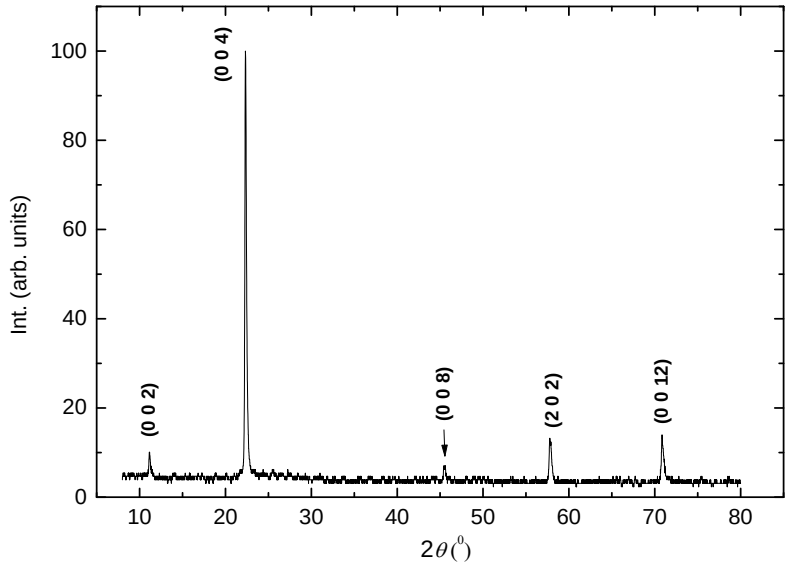

Fig. 1. XRD patterns of the primary GaSe single crystals.

2θ angular positions of diffraction lines and their relative intensities, along with respective Miller indices, are listed in Table 1.

Table 1 Structural parameters of primary GaSe single crystals

Experimental Values		**ICDD-JCPDS cards**			
2θ (°)	***I* (a. u.)**	**PDF**	**2θ (°)**	***I***	***h k l***
11.24	10.1	GaSe/37-0931(hex)	11.10	62	0 0 2
22.43	100	GaSe/37-0931(hex)	22.27	100	0 0 4
45.58	7	GaSe/37-0931(hex)	45.66	10	0 0 8
57.89	12.4	GaSe/37-0931(hex)	57.97	27	2 0 2
70.85	14	GaSe/37-0931(hex)	71.08	17	0 0 12

X-ray diffraction patterns of GaSe exhibit the intense characteristic (004) diffraction line and four low-intensity peaks labeled as (0 0 2), (0 0 8), (2 0 2), and (0 0 12). From the XRD patterns, hexagonal lattice parameters were found to be a=3.75 Å and c=15.85 Å and correspond to ε-GaSe modification.

Fig. 2 shows the XRD patterns of the composite obtained by a 24-h heat treatment of GaSe plates at 833 K in a Zn vapor atmosphere.

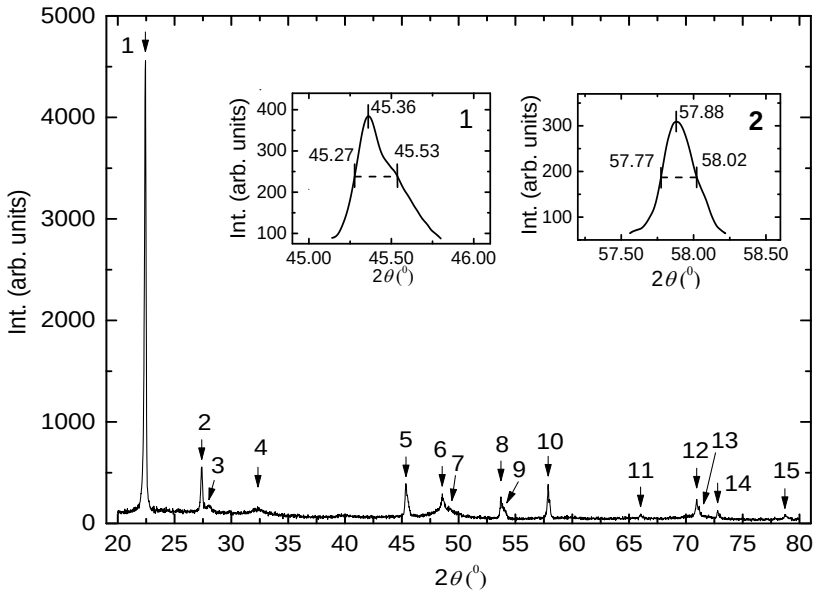

Fig. 2. X-ray diffraction pattern of the composite obtained by Zn-vapor heat treatment of the GaSe plates at 833 K for 24 h. Inset 1 shows the XRD line contour with 2θ = 45.36° from the planes with Miller indexes (2 2 0) of the ZnSe lattice. Inset 2 shows the XRD line contour with 2θ = 57.88° from the planes with Miller indexes (2 0 2) of the GaSe lattice.

It is evident from Fig. 2 that the XRD patterns of the composite (24-h heat treatment of GaSe plates in Zn vapors at 833 K) contains, in addition to characteristic lines of GaSe, a series of supplementary reflections, which are listed in Table 2.

Fig. 2 and Table 2 suggest that the supplementary XRD lines can be attributed to the (1 1 1), (2 2 0), (3 1 1), and (3 3 1) lattice planes of ZnSe formed by reaction of Zn atoms with Se atoms from the outer atomic planes of Se–Ga–Ga–Se packages. The (3 1 1) and (3 3 1) lines display a relatively wide contour (Fig. 2, insets 1 and 2), which indicates small sizes of the diffracting crystallites.

Crystallite mean size (D) was estimated by means of the Debye–Scherrer formula [12]

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

where λ is X-ray wavelength, θ represents the Bragg diffraction angle, and β denotes the angular full width at half maximum (FWHM) intensity. For $\beta = 4.55 \times 10^{-3}$ and $2\theta = 45.36°$, from the above formula, an average ZnSe crystallite size of ~45 nm was found. By using the same relation for the line located at $2\theta = 57.88°$, a value of ~63 nm is obtained for the crystallite size of GaSe from the composite.

Microcrystallites on the outer surface of the ZnSe–GaSe composite act as light diffusion centers, which do not allow direct measurement of linear reflectance and optical transmittance of the composite plates.

The spectral dependence of absorption coefficient for the ZnSe–GaSe composite plates was determined from diffuse reflection measurements using the Kubelka –Munk function [13]:

$$F(R_\infty) = \frac{\alpha}{S} = \frac{(1 - R_\infty)^2}{2R_\infty} \tag{2}$$

where α is the absorption coefficient, S is the light diffusion coefficient (depends on wavelength and size of diffusing particles), and R_∞ is the diffuse reflection coefficient.
The optical transition type and associated band gap of the semiconductor material can be determined via analyzing the following function [14]:

$$(F(R_\infty)\cdot h\nu)^2 = (h\nu - E_g)^n \quad (3)$$

where n = 2 and 1/2 for indirect and direct allowed optical transitions, respectively.

Table 2 Structural parameters of GaSe plate, heat treated for 24 h in Zn vapors, at 833 K.

	Experimental Values		ICDD-JCPDS cards				
No.	**2θ (^{0})**	***I* (a. u.)**	**PDF**	**2θ (^{0})**	***I***	***h k l***	***Compound***
1	22.44	4558	PDF 811971	22.338	99.9	0 0 6	GaSe
2	27.38	556	PCPDFWINv.2.3	27.223	100	1 1 1	ZnSe
3	28.02	182	PDF 781927	28.013	6.5	1 0 1	GaSe
4	32.34	160	PDF 370931	32.328	5	1 0 3	GaSe
5	45.36	392	PCPDFWINv.2.3	45.231	7.0	2 2 0	ZnSe
6	48.56	292	PDF 370931	48.583	17	1 1 0	GaSe
7	49.12	172					
8	53.72	262	PCPDFWINv.2.3	53.645	44	3 1 1	ZnSe
9	53.86	194	PDF 781927	53.969	28.0	1 1 4	GaSe
10	57.88	384	PDF 811971	57.725	4.8	2 0 2	GaSe
11	66.02	94					
12	70.96	238	PDF 781927	70.961	7.4	1 0 11	GaSe
13	71.18	170	PDF 370931	71.088	17	0 0 12	GaSe
14	72.80	128	PCPDFWINv.2.3	72.731	13	3 3 1	ZnSe
15	78.72	90	PDF 811971	78.722	3.2	1 2 2	GaSe

Fig. 3 shows the $(F(R_\infty)\cdot h\nu)^2$ dependence on the photon energy for the as prepared composite.

It is evident from this figure that two linear portions are clearly pronounced: one is located in the region of 1.9−2.2 eV, while the other lies in a range of 2.5−3.0 eV.

By extrapolating these linear parts to $(F(R_\infty)\cdot h\nu) = 0$, the optical band gap of semiconductor material for respective spectral domains can be determined according to Eq. (3); in this way, a value of 1.99 eV, which corresponds to GaSe single crystals, and 2.56 eV, which is in good agreement with the band gap of ZnSe in thin films [15, 16], have been found.

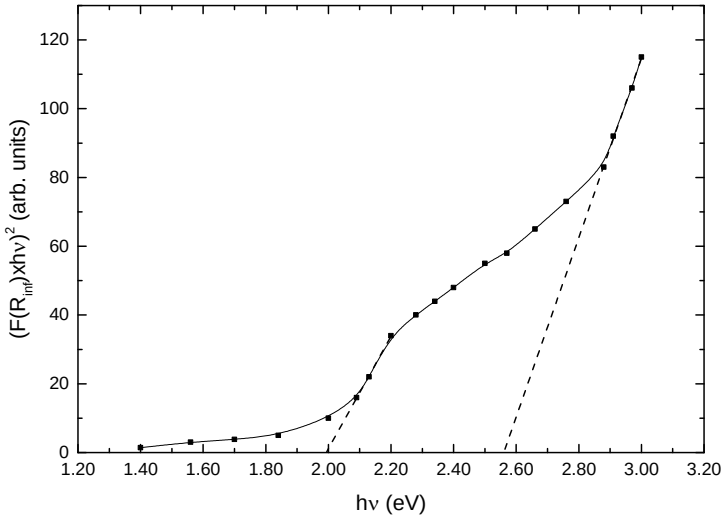

Fig. 3. $(F(R_\infty) \cdot \mathbf{h\nu})^2$ dependence on photon energy for the as prepared composite material.

Fig. 4 shows the PL spectrum recorded at T = 80 K from the (0001) surface of the heat-treated GaSe single-crystal plate.

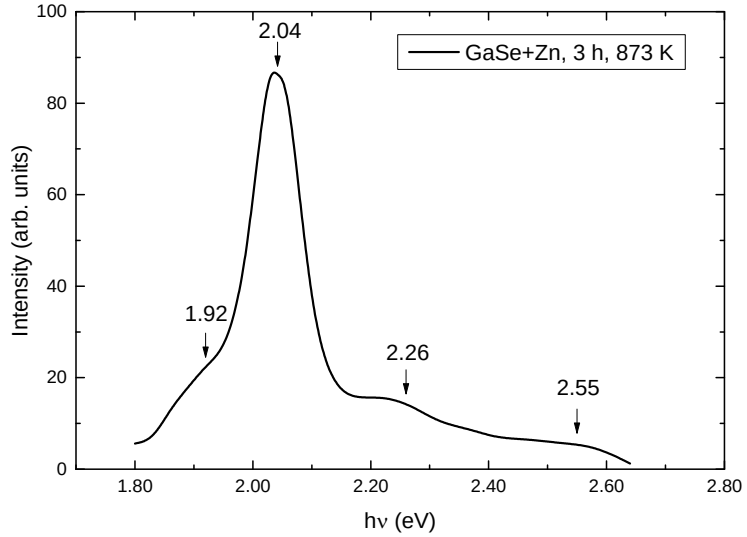

Fig. 4. PL spectrum recorded at 80 K from the (0 0 0 1) GaSe surface heat-treated in Zn vapors at 873 K for 3 h.

It is known that the PL spectrum recorded at 80 K corresponding to the (0 0 0 1) natural surface of GaSe single crystals contains the emission line of bound direct excitons, with a maximum at 2.098 eV, and two low intensity emission bands of indirect excitons, at 2.04 eV, as well as phononic repetitions of the bound exciton lines [17, 18].

At the same time, (Zn, Cd) doping concentrations up to 0.5 at % are known to produce PL quenching and create PL impurity bands in a photon energy region of 1.25−1.80 eV [19−21].

It is evident from Fig. 4 that the PL spectrum from the (0 0 0 1) surface of the GaSe plates covers a wide range of photon energies, from 1.80 eV to 2.64 eV, with a predominant maximum at 2.04 eV and three low intensity bands localized at 1.92, 2.26, and 2.55 eV. This structure can

be explained if we assume that a polycrystalline ZnSe layer is formed at the surface of the heat-treated GaSe plate in Zn vapors, which is capable of producing a PL emission. Taking into account that the energy gap of ZnSe at 78 K is E_g = 2.812 eV, from the PL spectrum (Fig. 4), it can be assumed that the PL emission of the ZnSe layer formed on the GaSe surface is determined by deep recombination levels. The PL bands with a maximum at 2.26 eV (green) and 2.042 eV (orange) are well known as characteristic emission bands of ZnSe single crystals at 78 K.

Fig. 4 shows that the PL spectrum is dominated by the emission band with a maximum at 2.042 eV, which is considered [22, 23] as a self-activated band. In this spectral region, a low intensity emission band of GaSe indirect excitons is also present [17], which is preceded by an intense PL band of direct localized excitons, with a maximum at 2.098 eV. The absence of a direct exciton emission line in the composite material (Fig. 4) indicates the presence of structural defects in GaSe crystals from the composite, which effectively shield the electron–hole bonds. It is evident from Fig. 4 that FWHM of the PL band with a maximum at 2.042 eV is ~0.12 eV; therefore, it *cannot* be associated with the excitonic emission in GaSe crystals from the composite.

It is also known that low Cu and Cd impurity concentrations (≤0.01at %) in GaSe lead to the formation of a PL band at 1.90 eV, which allows us to state that the impurity PL band with a maximum at 1.92 eV can be attributed to the luminescent emission of the ZnSe–GaSe composite.

4. Conclusions

Heat treatment of single crystalline GaSe plates in Zn vapors leads to the formation of a ZnSe layer on the outer surface of GaSe, while Zn intercalated atoms between the Se atomic planes of layered Se–Ga–Ga–Se packages give rise to nanocrystalline ZnSe layers inside the GaSe plates.

GaSe and ZnSe micro- and nanocrystallites act as light diffusion centers for the spectral region from the vicinity of the fundamental absorption threshold of these materials. The absorption spectrum from this spectral range was calculated using the empiric Kubelka-Munk formula. Analysis of the absorption spectrum of the composite reveals two major contributions—of the ZnSe (E_g = 2.56 eV) and GaSe (E_g = 1.99 eV) crystallites—at room temperature.

The PL spectrum of the ZnSe–GaSe composite surface is determined by the luminescent emission of the ZnSe layer from the outer surface of plates, in which, together with characteristic ZnSe bands (2.26 and 2.042 eV), an impurity band of the GaSe crystals with a maximum at 1.92 eV is observed.

References

[1] A. Castellano, Appl. Phys. Lett. 48 (4), 298 (1986).
[2] E. Bringuier, A. Bourdon, N. Piccioli, and A. Chevy, Phys. Rev. B 49, 16971, (1994).
[3] Ch. Ferrer-Roca, J. Bouvier, A. Segura, M. V. Andrés, and V. Muñoz, J. Appl. Phys. 85 (7), 3780, (1999).
[4] L. Yan-Zhao, W. Xin-Bing, M. Liang, Z. Du-Luo, and C. Zu-Hai, Chin. Phys. Lett. 28 (3), 034201 (2011).
[5] Y. Depeursinge, Il NuovoCimentoB 64 (1), 111, (1981).
[6] F. O. Ivashchishin and I. I. Grygorchak, Phys. Solid State 52 (10), 2026, (2010).
[7] Z. D. Kovalyuk, V. B. Boledzyuk, V. V. Shevchyk, V. M. Kaminskii, and A. D. Shevchenko,

Semiconductors 46 (8), 971, (2012).
[8] C. M. Julien and M. Balkanski, Mater. Sci. Eng. B 100 (3), 263, (2003).
[9] C. M. Julien, Mater. Sci. Eng. R 40 (2), 47, (2003).
[10 Z. D. Kovalyuk, M. M. Pyrlya, and V. B. Boledzyuk, J. Optoelectron. Adv. Mater. 5(4), 869, (2003).
[11] V. P. Savchyn and V. B. Kytsai, Thin Solid Films, 361–362, 123, (2000).
[12] W.-.F. Wu and B.-S. Chiou, Thin Solid Films, 298, 221, (1997).
[13] S. I. Boldish and W. B. White, Am. Mineral. 83, 865, (1998).
[14] J. Tauc, Amorphous and Liquid Semiconductors, Plenum, New Zork, 1974 (Chapter 4).
[15] R. Le Toullec, N. Piccioli, M. Mejatty, and M. Balkanski, Nuovo Cimento 38B, 159, (1977).
[16] R.K. Swank, Phys. Rev. 153, 844, (1967).
[17] V. Capozzi, Phys. Rev. B 28(8), 4620, (1983).
[18] V. Capozzi and A. Minafra, J. Phys. C: Solid State Phys. 14, 4335, (1981).
[19] S. Shigetomi, T. Ikari, and H. Nakashima, J. Appl. Phys. 74, 4125, (1993).
[20] S. Shigetomi, T. Ikari, and H. Nakashima, Phys. Stat. Sol. (a), 160, 159, (1997).
[21] S. Shigetomi, T. Ikari, and H. Nishimura, J. Appl. Phys. 69, 7936, (1991).
[22] G. B. Stringfellow and R.H. Bube, Phys. Rev. 171, 903, (1968).
[23] S. Iida, J. Phys. Soc. Jpn. 25 (1), 177, (1968).