Photoluminescence of CdGeP$_2$ and (Cd,Mn)GeP$_2$

G.A. Medvedkin [a,*], V.M. Smirnov [a,b], T. Ishibashi [c], K. Sato [c]

[a] *Solid State Physics, Ioffe Physico-Technical Institute, 26 Polytechnicheskaya Street, St Petersburg 194021, Russian Federation*
[b] *Physics Department, Lancaster University, Lancaster LA1 4YB, UK*
[c] *Tokyo University of Agriculture and Technology, Tokyo 184-8588, Japan*

Abstract

Photoluminescence of CdGeP$_2$ (112) single crystal and CdGeP$_2$ epitaxial film grown on GaAs (001) substrate have been studied and their spectral similarity found. Spectral bands associated with donor/acceptor transitions peak at close energies for both substances and all are lower than the energy gap of the chalcopyrite crystal.

On the other hand, the growth of (Cd,Mn)GeP$_2$ ferromagnetic layer on CdGeP$_2$ (112) single crystal was performed to make it possible observation of PL from both the ferromagnetic layer and substrate. The green laser excitation (514, 532 nm) produces a proper photoluminescence similar to that in the undoped CdGeP$_2$ crystal and film. An extra emission from the ferromagnetic–nonmagnetic heterojunction occurs to extend up to photon energies exceeding E_g of the host semiconductor. The short wavelength photoluminescence is to be due to (Cd,Mn)GeP$_2$ dilute magnetic semiconductor (DMS). This fact states that Mn-doped II–IV–V$_2$ chalcopyrites are closer to II–VI DMS than to another group III–V DMS, where the heavy Mn-doping suppresses photoluminescence at all. Features of the observed short wavelength emission are discussing based on the temperature and spectral analyses.
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1. Introduction

The progress of spintronic devices goes on a way of adoption of advantages cumulated by customary electronics and optoelectronics [1]. The polarized light can give means to govern a spin orientation [2], so optoelectronic devices based on GaAs–GaMnAs system attract the great attention [3,4]. There are two main disadvantages in this system as low equilibrium solubility of Mn in GaAs and the incorporated Mn serves as known as a killer of emission processes inside the ferromagnetic GaMnAs. It stimulates search of a new diamond-like semiconductor, which can overcome these difficulties. The promising materials with nearest optoelectronic properties to III–V binary compounds are II–IV–V$_2$ ternary compounds, in part a direct-gap CdGeP$_2$. This ternary chalcopyrite compound and other II–IV–V$_2$:Mn compounds have recently shown room-temperature ferromagnetism exceeding the other III–V and II–VI binary compounds by Curie temperature [5–9]. The chemical advantage of II–IV–V$_2$ chalcopyrites is the natural ability to adopt a high concentration of manganese into tetrahedral node positions of the crystal lattice. The present paper reports first photoluminescence (PL) results demonstrating what advantage in emission can give Mn incorporated into CdGeP$_2$ crystals.

2. Experimental

The (112) oriented single crystals of CdGeP$_2$ were cut from the ingot grown by the directional crystallization technique of the stoichiometric melt. Samples were oriented by X-ray diffraction, then polished mechanically and cleaned chemically. The epitaxial films of a composition close to CdGeP$_2$ were grown on GaAs (100) substrate using the metal-organic molecular beam epitaxy (MBE). MBE equipment was supplied with sources of elements: Cd flux (2–4×10^{-6} Torr), Ge flux (1–4×10^{-8} Torr) using Knudsen cells, and for P$_2$ (1.6 sccm)—the gas flux decomposed from *tert*-butyl phosphine (TBP) using a cracking cell at $T=813$ °C. The first stage of growth started from self-organizing nucleation over the surface of GaAs. Because the crystal lattice parameters of two materials differ a little ($a=5.741$ Å, $c/2=5.388$ Å, and $a=5.653$ Å, accordingly), the growth on (100) surface of GaAs goes preferably in more favorable way of islands. Then islands increase in size and reach a micron dimension in diameter.

* Corresponding author. Tel.: +7 812 247 9138; fax: +7 812 247 1017.
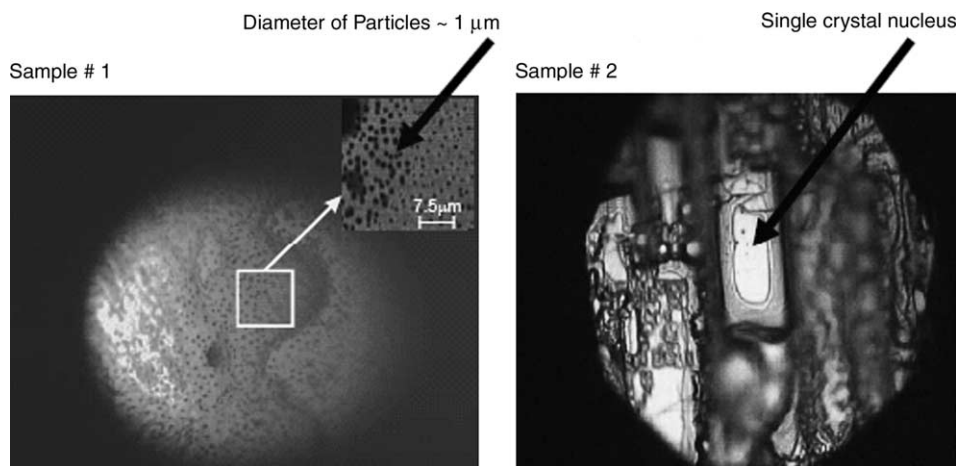*E-mail address:* g.a.medvedkin@mail.ioffe.ru (G.A. Medvedkin).

Fig. 1. Optical microscopy and SEM control of the surface. Sample #1—optical and SEM (insert) images of CdGeP$_2$ layer surface. Sample #2—a number of crystal nuclei is imprinted on the surface through an optical microscope.

Optical and scanning electron microscopic images were used for a surface control.

The growth of Mn diffusion layer on the (112) surface of CdGeP$_2$ single crystal was carried out in the MBE chamber with a residual pressure of 10^{-9} Torr. Metallic manganese was deposited on the crystal and diffused for the annealing at 550 °C for 30 min. So, approximately a micron thick layer of (Cd,Mn)GeP$_2$ DMS was obtained with an optically acceptable surface. Ferromagnetic and magneto-optical properties of these layers were reported earlier [5–8]. Photoluminescence spectra were measured at low and high temperatures 10, 20 and 300 K in the He-closed loop cryostat under excitation by green lines of YAG–SHG laser (532 nm, 40 mW) and Ar$^+$-ion laser (514 nm, 0.75 W).

3. Results and discussion

Fig. 1 presents photographs of two samples of CdGeP$_2$ films grown by MOMBE on (001) GaAs substrates. Microscopic investigations found crystalline areas in the film with a certain crystallite orientation (along the substrate plane). At the first stage CdGeP$_2$ can crystallize as nano-size crystallites with a self organized order over the GaAs surface. Then the growth of larger crystal nuclei was checked through an optical microscope. Note, the single crystal growth of CdGeP$_2$ compound started on GaAs substrate, but it was hard to grow the flat uniform layer over the whole surface because of the lattice mismatch ($\delta a = 2\Delta a/\Sigma a = -1.46\%$, and $+4.8\%$ in c-direction). In spite of that fact the film shows some islands, the crystal quality of every crystal island is suggested high.

Fig. 2 shows PL of the undoped CdGeP$_2$ single crystal as compared with the undoped CdGeP$_2$ thin film grown on GaAs. Excitation by the green laser and experimental conditions for both samples were equivalent. The main PL bands in the range of 0.8–1.6 eV occur to be similar by a spectral position. All the emission bands are situated at energy lower than E_g of CdGeP$_2$ and can be associated with optical transitions through donor and acceptor levels. The 1.5 eV band is predominant in both crystal and film samples. The 1.65 eV band disappears in

the film but the long-wavelength band become stronger and sharper. We cannot completely exclude an influence of GaAs substrate on PL spectra, however, it is more likely the observed PL bands belong to CdGeP$_2$ since their spectral position and intense behavior are in agreement with that measured on undoped and In-doped CdGeP$_2$ crystals [10,11] grown by the method of zone recrystallization. An attribute to the ternary compound is proven by the following spectral analysis. The curves presented in Fig. 2 were treated by a deconvolution treatment using the Gaussian multipeak fit, and results are given in Table 1. The individual PL bands have close energy positions for both the crystal and film. Peaks 2 to 5 exhibit additionally comparable spectral widths and areas. This analysis points out the close similarity in emission properties of the film and bulk crystal.

Introduction of the transition metal impurity Mn into a diamond-like semiconductor results in paramagnetic or spin-glass state (mostly for II–VI compounds) and paramagnetic or ferromagnetic state (mostly for III–V compounds). Ternary chalcopyrite II–IV–V$_2$ compounds combine properties of the above groups of binaries, i.e. Mn introduction into the ternary
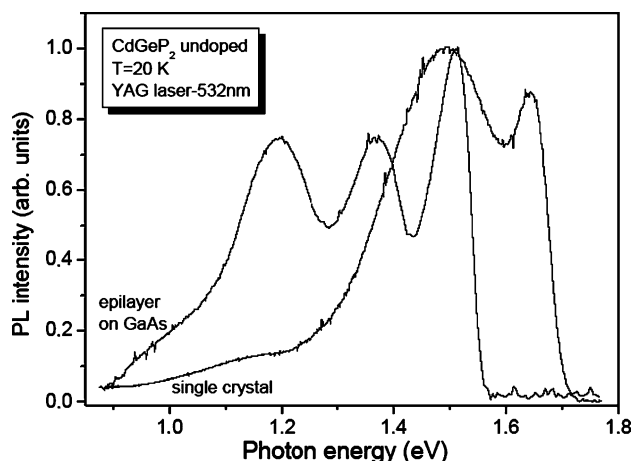

Fig. 2. PL spectra of undoped CdGeP$_2$ single crystal and epitaxial layer on GaAs.

Table 1
Comparison of spectral parameters by the Gaussian fit for CdGeP$_2$ (crystal/layer)

Peak	Center (eV)	Area	Width	Height
1	1.645/–	0.06/–	0.072/–	0.665/–
2	1.51/1.51	0.172/0.068	0.145/0.057	0.846/0.947
3	1.38/1.377	0.067/0.114	0.137/0.128	0.438/0.709
4	1.2/1.195	0.023/0.117	0.157/0.129	0.126/0.717
5	1.02/1.026	0.019/0.038	0.24/0.152	0.053/0.2

compound proceeds just as in II–VI from 0 to 100% (due to the II-group site), and Mn serves as an acceptor like that in III–V compounds [12–14]. This combination leads to ferromagnetism at a rather higher Curie temperature exceeding that in III–V DMS compounds ($T_C = 150$ K for GaMnAs). However, excellent optical emission properties of CdMnTe type DMS will diminish dramatically in passage to GaMnAs type DMS even if several percentage of Mn are introduced. Generally, transition metals are hardly adopted in III–V solid solutions and the Mn^{2+} valence state at the III-group site is out of simple equilibrium. That is why, the optical band edge is stretched out in the forbidden gap and nobody can before observe any proper PL from GaMnAs. Using the Mn-doped II–IV–V$_2$ compounds, we hope to solve a problem of strong suppression of PL in ferromagnetic diamond-like semiconductors.

Fig. 3 demonstrates PL spectrum of the starting undoped CdGeP$_2$ crystal with individual spectral maximums by fitting. The mark A denotes a minimal direct optical transition in CdGeP$_2$ at low temperature and the insert shows a scaled decrease in PL intensity near the band gap. One can see an absence of emission at energy > 1.74 eV, lower E_g, that is typical for compensated compound semiconductors with point defects. We intended investigation with a specially prepared cleaned surface of CdGeP$_2$ crystals, but were failed to observe any emission in the range near a minimum A-transition.

Another effect was produced by the manganese incorporation. Fig. 4 presents two PL spectra of (Cd,Mn)GeP$_2$ DMS layer prepared by the reactive Mn-diffusion into the undoped CdGeP$_2$ oriented crystal [5]. Under excitation of the green laser with a rather intense pumping (0.75 W) we succeeded in
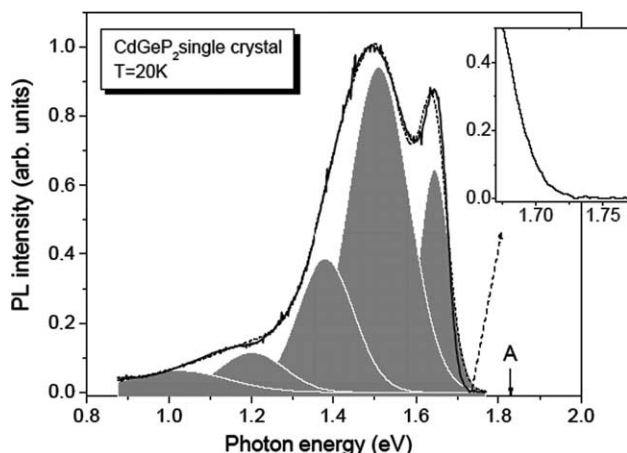

Fig. 3. Multipeak spectral Gaussian fit for PL spectra of CdGeP$_2$ crystal. Insert—the short wavelength tail.
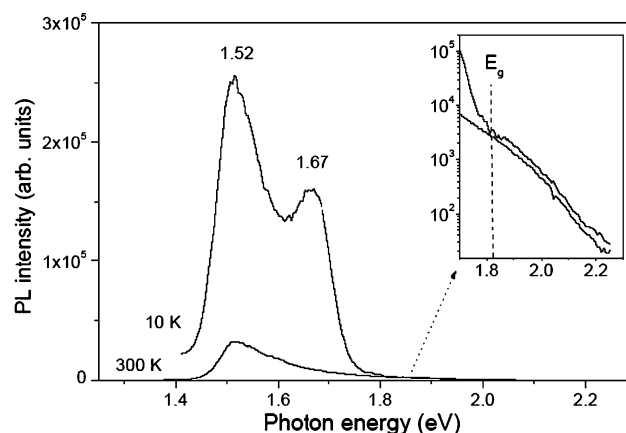

Fig. 4. PL of (Cd,Mn)GeP$_2$ layer on CdGeP$_2$ crystal at $T = 10$ and 300 K. Excitation Ar-ion laser (514 nm, 0.75 W). Insert—the corresponding short wavelength tails at energy $> E_g$.

observation of short-wavelength emission. A distinct spectral wing in the range of 1.8–2.2 eV is shown in the insert to Fig. 4. All the optical emission of this wing is concentrated at energies considerably higher the band gap of CdGeP$_2$, $A = 1.83$ eV. The spectral wing has an extended shape (not a Gaussian/Lorenzian decay) with a spectral weight around 2.0 eV. Although the PL bands at 1.52 and 1.67 eV decrease with increasing temperature to 300 K, the spectral wing remains approximately the same by intensity and shape. This fact points out Mn intra ion transitions are likely, but for sure a variable composition by Mn-diffused distribution exists, so it causes a varying energy gap. Thus, this study confirms the earlier established enlargement of the gap of CdGeP$_2$ after incorporation of the magnetic impurity Mn into the chalcopyrite lattice at Cd-site predominantly [5,8].

The next point of the study concerns a surprising property of the ferromagnetic chalcopyrite (Cd,Mn)GeP$_2$, whose emission retains after incorporation of a high concentration of manganese into the host undoped CdGeP$_2$ in contrast to III–V binary analogs heavily Mn-doped. It is known that manganese serves a killer of PL in GaMnAs epitaxial layers grown on GaAs at as low as [Mn] = 2–3%. The investigated (Cd,Mn)GeP$_2$ layers contained ~ 20% Mn on average at thickness of ~ 0.4 μm. We confidently observed PL from this DMS layer at energies of 1.8–2.2 eV in the temperature range $T = 10$–300 K. Furthermore, the tested samples (Cd,Mn)GeP$_2$/CdGeP$_2$ emitted such kind PL at $E > E_g$ (1.8 eV) for a long period of time, at least for 3 years. No temperature dependence was observed for the short-wavelength band as shown in Fig. 3. This can indicate the emission goes from the Mn-diffused layer of DMS with a variable Mn-concentration and due to smoothly changeable the energy gap in depth. Early experiments with the UV excitation by 325-nm He–Cd laser [5] demonstrated a series of PL peaks in the interval of 2.5–3.5 eV. The observed PL maximums can be satisfactorily ascribed to intra ion transitions in manganese and fit well by the Tanabe–Sugano diagram [15]. This diagram was developed for 3d^5 shell of Mn^{2+} ion in the crystal field of T_d symmetry. The tetragonal crystal field of chalcopyrite D_{2d}^{12} causes a small

perturbation in the cubic symmetry and it allows usage of the Tanabe–Sugano diagram for II–IV–V_2 diamond-like crystals as well. Recently EPR and SQUID investigations have found that Mn exhibits properties of isolated centers when diffused into the chalcopyrite $ZnGeP_2$ and simultaneously forms a ferromagnetic layer of $(Zn,Mn)GeP_2$ [13,16]. Furthermore, the ferromagnetic coupling retains even in a deep situated DMS [17]. The finding gives a chance to consider Mn inter ion transitions in $CdGeP_2$ over the entire spectral range with the model diagram of Tanabe–Sugano, beginning from ~ 2.0 eV. However, because of a perceptible influence of other effects (variable Mn concentration in depth and fluctuations) we can observe only a weak manifestation of this minimum intra ion transition around 2.0 eV.

4. Conclusion

Photoluminescence measurements under the green laser excitation show a proper emission from both nonmagnetic $CdGeP_2$ film grown on GaAs and ferromagnetic $(Cd,Mn)GeP_2$ film grown on the undoped $CdGeP_2$ crystal. Comparison of undoped films with crystals demonstrates similarity of their PL spectral bands and suggests equivalent substance of $CdGeP_2$. All emissions from the undoped film and bulk crystal are located lower the energy gap, corresponding to optical transitions through donor and accentor defect centers.

Introduction of manganese into $CdGeP_2$ substrate gives rise to extension of PL spectrum up to 2.2 eV that proves the enlargement of E_g in the ferromagnetic $(Cd,Mn)GeP_2$ as compared to the host $CdGeP_2$. The short wavelength emission is to be due to manganese incorporated into $(Cd,Mn)GeP_2$ DMS layer. This fact states that Mn-doped II–IV–V_2 chalcopyrites are closer to II–VI DMS than to III–V DMS, where the heavy Mn-doping kills PL emission completely.

Acknowledgements

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