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# Photoluminescence of $CdGeP_2$ and (Cd,Mn)$GeP_2$

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## 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.


*Keywords:* A. Magnetic materials; B. Epitaxial growth; D. Luminescence

## 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 ($2–4\times10^{-6}$ Torr), Ge flux ($1–4\times10^{-8}$ 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.

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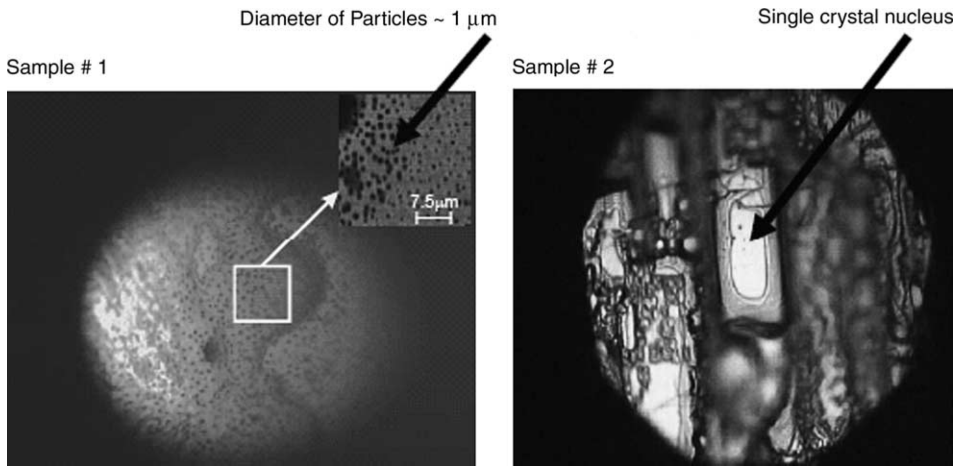


Fig. 1. Optical microscopy and SEM control of the surface. Sample #1—optical and SEM (insert) images of $CdGeP_2$ layer surface. Sample #2—a number of crystal nuclei is imprinted on the surface through an optical microscope.

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

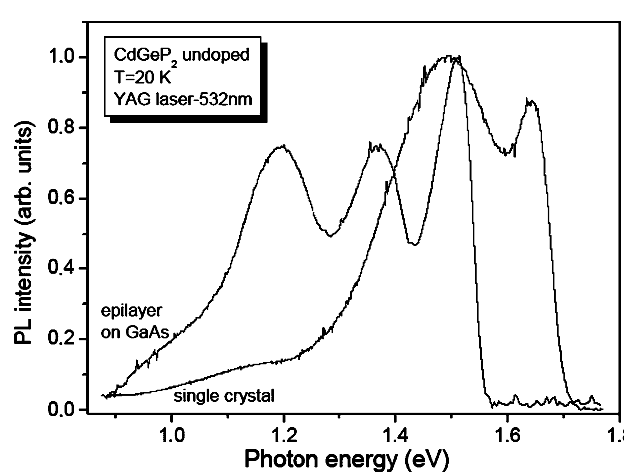


Fig. 2. PL spectra of undoped $CdGeP_2$ single crystal and epitaxial layer on GaAs.