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Express Letter

Room Temperature Ferromagnetism in Novel Diluted Magnetic Semiconductor $Cd_{1-x}Mn_xGeP_2$

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High concentration of Mn atoms has been incorporated in the surface region of II-IV-V_2 type chalcopyrite semiconductor $CdGeP_2$. Photoluminescence spectrum at 20 K shows a peak around 3.2 eV, suggesting that the incorporation of Mn introduces an energy gap much higher than that of the host semiconductor ($E_g = 1.83$ eV). Prominent magnetic hysteresis loops with coercivity of 0.5 kOe has been observed at room temperature. Magnetic force microscope (MFM) measurements reveal a stripe-shaped domain pattern on the top surface. Magneto-optical Kerr ellipticity spectrum measured at room temperature show a prominent peak at 1.7 eV and a broad tail up to 3.5 eV. We tentatively attribute the ferromagnetism to the double exchange interaction between Mn^{2+} and Mn^{3+} states due to the structural feature of II-IV-V_2 type chalcopyrite compounds.

KEYWORDS: $Cd_{1-x}Mn_xGeP_2$, diluted magnetic semiconductor, chalcopyrite structure, ferromagnetism, magnetic force microscopy, magneto-optical spectrum

1. Introduction

History of magnetic semiconductors started in late 1960's aiming at realization of new functionality by combining electrical transport and magnetism. In spite of numerous studies carried out on Eu-chalcogenides[1] (*e.g.*, EuSe, EuS, EuO) and Cr-chalcogenide spinels[2] (*e.g.*, $CdCr_2Se_4$, $CdCr_2S_4$), no practical application of magnetic semiconductors has been realized. Most of the reason that hampered application may be a low Curie temperature of these materials.

Diluted magnetic semiconductors (DMS) based on II-VI compounds[3] (*e.g.*, $Cd_{1-x}Mn_xTe$) appeared in early 1980's. Although a lot of fundamental studies have been carried out in this type of DMS, little application has been realized, except for optical isolators utilizing the large Verde constant of DMS in the region of the optical absorption edge.[4] This is due to the fact that most of the II-VI-based DMS are paramagnetic or spin glass.

On the contrary, III-V semiconductor-based DMS's have been attracting interest as promising materials for new spin electronic devices, because they show ferromagnetism, whose T_c depends on the carrier concentration.[5] Higher T_c is predicted theoretically only if carrier concentration is effectively raised. However, the highest Curie temperature T_c obtained to date is about 110 K in $Ga_{1-x}Mn_xAs$. For practical applications, room temperature ferromagnetism is strongly required.

Recently, theoretical approach based on the first principle calculation predicts that high T_c ferromagnetism can be realized in Mn-doped ZnO magnetic semiconductor.[6] Since the proposed ferromagnetism is the consequence of double exchange interaction between Mn^{2+} and Mn^{3+} ions, heavy p-type doping is necessary. To solve the difficulty in preparation of p-type ZnO, co-doping process has been proposed.[7]

Compared with ZnO, p-type doping is comparably easier in ternary semiconductors with the chalcopyrite type structure. Moreover, high carrier mobility, which is important for device applications, has been reported in II-IV-V_2 type chalcopyrite semiconductors. Compared with III-V semiconductors, whereas Mn^{2+} should occupy the group III sites, Mn^{2+} can easily substitute for the group II site without any sacrifice of electric neutrality. If a part of the Mn atoms occupy the group IV site, they will act as acceptors to supply holes to the Mn 3d band making the Mn ions partially trivalent, which may realize the Mn^{2+}-Mn^{3+} double exchange mechanism. Based on this postulation, we tried an incorporation of Mn atoms into the ternary chalcopyrite type semiconductor $CdGeP_2$, and carried out crystallographic as well as magnetic and magneto-optical characterization.

2. Experimental

$CdGeP_2$ crystallizes in tetragonal chalcopyrite structure with lattice constants of $a = 0.5741$ nm and $c = 1.0775$ nm, and u-parameter of 0.282. The energy gap is 1.72 eV (300 K) and 1.83 eV ($\leq$80 K). Both n and p conductivity types were reported, with the mobility 1500 $cm^2/V{\cdot}s$ and 90 $cm^2/V{\cdot}s$, respectively. Single crystal of $CdGeP_2$ has been grown at the Ioffe Institute by directional crystallization. The flat-parallel crystal plate had nearly rectangular shape with size of 3×5 mm^2.

In order to prepare $Cd_{1-x}Mn_xGeP_2$ solid solution (hereafter referred to as $CdMnGeP_2$), the solid phase chemical reaction technique was employed. The single crystal of $CdGeP_2$ was used as a host material. Prior to the reacting process the surface of the crystal was polished and etched with Br-methanol solution. The specimen was introduced into the molecular beam epitaxy chamber with the residual pressure of 1.4×10^{-8} Torr. Vacuum deposition of Mn layer on the single crystal surface followed by the solid phase reaction at elevated temperatures was carried out in the chamber. The specific technological details will be described elsewhere.

During the deposition-reaction procedure the surface was monitored using the reflection high-energy electron diffraction (RHEED). Before the Mn-deposition, RHEED pattern close to that of (112) was observed indicating the high perfection of the crystal surface. The deposition of Mn layer leads to disappearance of the atomic order. After finishing the reacting process the original RHEED pattern is recovered with a trace of typical texture reflections. The thickness and composition for the prepared layers of $CdMnGeP_2$ were analyzed using a S-4500 field emission electron scanning microscope

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(FE-SEM) with the instrument EMAX-577OW. To check the layer structure, energy dispersive X-ray (EDX) analysis was done using the SEM.

Crystallographic analysis was carried out using a Rigaku RAD-IIC diffractometer. Detailed lattice constant change was investigated using a RIGAKU RAD-B with InP crystal monochromator. Photoluminescence (PL) spectrum was measured at 20 K using the 325-nm line of He-Cd laser. The emission was dispersed with a JASCO type CT50-C grating monochromator with a focal length of 500 mm.

The magnetization curve of the specimen was characterized using a vibrating sample magnetometer (VSM). The surface of the layer was characterized by atomic force microscope and magnetic force microscope. The magneto-optical Kerr ellipticity spectrum was measured by polarization modulation technique using the photoelastic modulator for photon energies between 1.2 eV and 4 eV.

3. Results and Discussion

Taking into account the ionic radii and valencies of Mn, Cd and Ge, we assume most of the Mn occupies the divalent Cd-site. The Mn/Cd ratio analyzed by EDX is shown in Fig. 1. The ratio at the surface reaches 53.4% and drops rapidly with depth, the value being 12.7% at 0.6 μm and 0.9% at 2.5 μm. The average Mn/Cd ratio is determined as 20% for effective thickness 0.5 μm.

The X-ray diffraction pattern of the grown layer shows no traces of extraneous phases such as MnP. We also found that the crystal structure of the grown layer does not strongly differ from the substrate $CdGeP_2$, except for the top-most surface in which a texture formation is confirmed. Detailed crystallographic analysis is underway and will be published in later publication.

The PL spectrum is given in Fig. 2, showing a broad emission band between 1.6 and 3.6 eV with a peak at 3.24 eV, which suggests that the new material $CdMnGeP_2$ grown on the crystal surface of the $CdGeP_2$ single crystal is also a semiconductor with an enlarged energy gap E_g relative to the gap (1.83 eV) of the host semiconductor. The distribution of the PL energy may correspond to the distribution of E_g from 1.8 eV of the host to 3.5 eV of the top surface layer. This fact can be associated with the distribution of Mn/Cd ratio from nearly zero (0.9%) at 2.5 μm to 53% at surface.

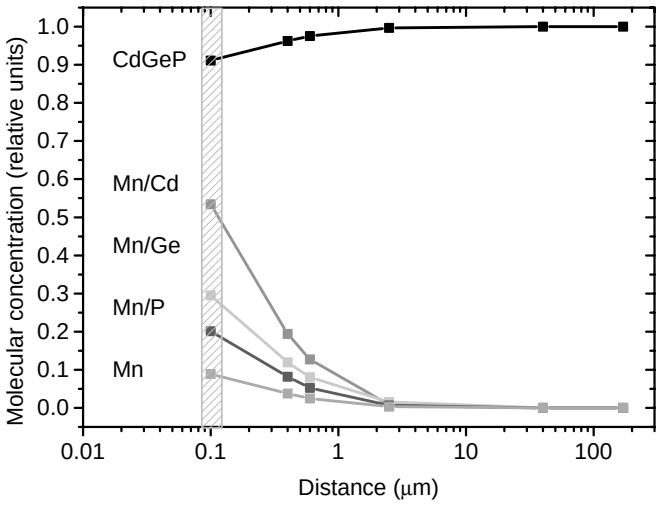

Fig. 1. Concentration profiles for chemical elements in $Cd_{1-x}Mn_xGeP_2$/$CdGeP_2$sample. The denotement of CdGeP corresponds to a sum of concentrations for three elements. The hatched strip conditionally shows the sample surface.

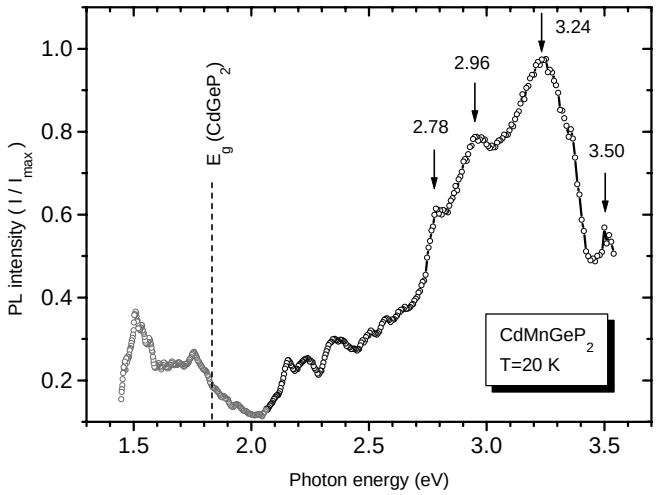

Fig. 2. Photoluminescence spectrum of $CdMnGeP_2$ layer. Excitation-He-Cd laser (325 nm, 100 mW).

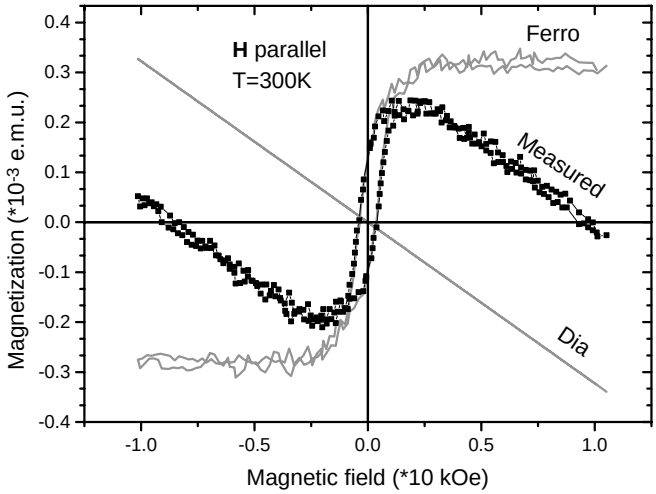

Fig. 3. Hysteresis loop for $Cd_{1-x}Mn_xGeP_2/CdGeP_2$ at room temperature. Two components (Ferromagnetic and Diamagnetic) are extracted from experimental curve (points).

The magnetization curve measured at room temperature is shown in Fig. 3. The curve is composed of diamagnetic and ferromagnetic components. The former may be attributed to the host substrate and the latter to the new DMS layer. The ferromagnetic component shows a well-defined hysteresis loop with the saturation field H_s of 2 kOe and coercivity H_c of about 0.5 kOe. The result clearly suggests that T_c is higher than room temperature. Determination of T_c is underway and will be presented in our later publication.

AFM and MFM images (8 μm × 8 μm) of the surface of the new DMS in the remanence magnetization state were measured at room temperature. As shown in Fig. 4, the MFM image clearly shows the stripe-shaped magnetic domain structure, the width of 1 μm that is considerably larger than the size of the texture (0.2 μm), supporting an existence of magnetization at the surface of the DMS layer.

The magnetooptical Kerr ellipticity η_K was measured

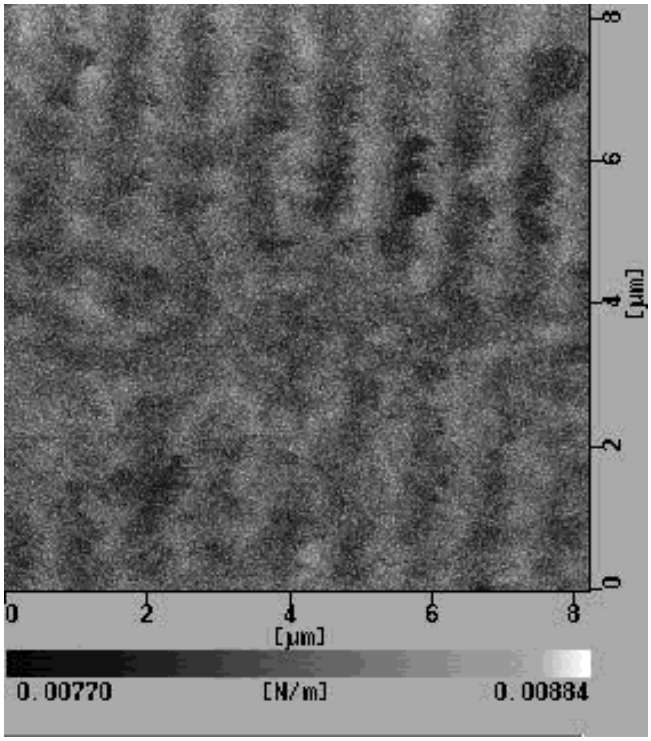

Fig. 4. The MFM image measured on the surface of the $CdMnGeP_2$ at room temperature.

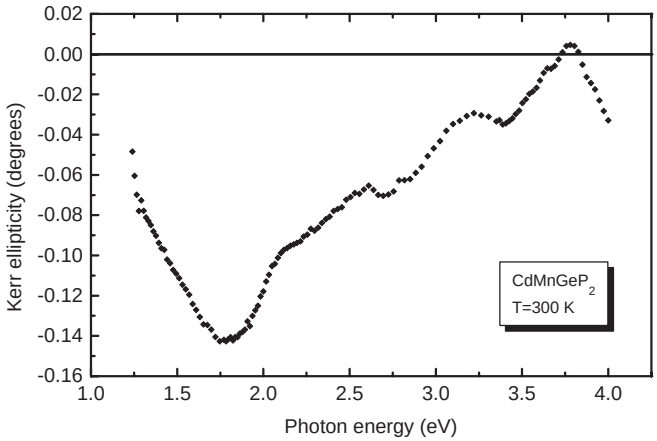

Fig. 5. The magnetooptical Kerr ellipticity of $CdMnGeP_2$ at room temperature.

at room temperature for photon energies between 1.2 and 4.0 eV. As shown in Fig. 5, the magnetooptical structure of η_K covers the photon energy region from 1.5 eV to 4.0 eV and shows a distinct peak around 1.75 eV, the energy gap of the material, followed by a broad tail up to 3.5 eV.

According to recent ab-initio band calculation carried out in Mn-doped II-IV-V_2 chalcopyrite such as $ZnGeAs_2$,[8] the ferromagnetic interaction due to the double exchange seems to be stabilized relative to the antiferromagnetic superexchange interaction. Therefore we believe ferromagnetism can occur commonly in Mn-doped II-IV-V_2 semiconductors.

4. Conclusion

We have fabricated a novel DMS based on the II-IV-V_2 chalcopyrite semiconductor, $CdMnGeP_2$. The band gap was found to be enlarged by two times compared with that of the host $CdGeP_2$. Ferromagnetic behaviors such as the magnetic hysteresis loop, the stripe domain pattern and the magnetooptical effect were observed at room temperature. These results suggest the first discovery of a room-temperature ferromagnetic semiconductor based on the chalcopyrite compound.

Acknowledgements

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