Ferromagnetic phenomenon revealed in the chalcopyrite semiconductor CdGeP2:Mn

Article *in* Journal of Applied Physics · July 2001

DOI: 10.1063/1.1357842 · Source: IEEE Xplore

Ferromagnetic phenomenon revealed in the chalcopyrite semiconductor $CdGeP_2$:Mn

Katsuaki Sato,[a] Gennadiy A. Medvedkin,[b] Takao Nishi, Youichi Hasegawa, Ryuji Misawa, Kanta Hirose, and Takayuki Ishibashi
Department of Applied Physics, Faculty of Technology, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184-8588, Japan

High concentration of Mn atoms has been successfully incorporated into the chalcopyrite type II–IV–V_2 semiconductor $CdGeP_2$ by solid-state reaction technique without causing any structural changes. Polycrystalline powder of the chalcopyrite-related material in Cd–Mn–Ge–P quaternary system has been additionally synthesized by sintering technology. Well-defined $M-H$ hysteresis loops were observed at room temperature in $CdGeP_2$:Mn single crystal and polycrystalline powder samples grown independently. The Curie temperature has been determined to be 320 K for single crystal phase $Cd_xMn_{1-x}GeP_2$ and 310 K for the polycrystalline powder. Magnetic force microscopy (MFM) observation clearly showed a stripe domain pattern on the Mn-diffused surface of $CdGeP_2$ single crystal. The magneto-optical Kerr ellipticity spectrum of $CdGeP_2$:Mn crystal showed a peak around 1.75 eV at $T=300$ K. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1357842]

Magnetic semiconductors have been attracting attention as suitable materials for spin-electronics applications, since they possess both ferromagnetism and electronic transport properties.[1,2] However, most of the magnetic semiconductors investigated to date show Curie temperature Tc far below the room temperature, which has been the main obstacle that hampers the practical application of magnetic semiconductors. The highest Tc reported to date for diluted magnetic semiconductors is 110 K for GaMnAs.[3] Therefore, realization of room temperature ferromagnetism has long been anticipated.

Here, we paid attention to II–IV–V_2 type chalcopyrite semiconductors, which are the ternary analogs of III–V compounds. We selected $CdGeP_2$ considering an ease of substitution of Mn for Cd element like in II–VI compounds. The $CdGeP_2$ semiconductor crystallizes in the tetragonal chalcopyrite structure with lattice parameters of $a=0.5741$ nm, $c=1.0775$ nm and $\mu=0.282$. The energy gap is 1.72 eV at room temperature.

Recently, we have found that high concentration of Mn atoms can be easily incorporated by the solid-state reaction into a single crystal of $CdGeP_2$ without changing the crystal structure and the Mn-incorporated layer shows a ferromagnetic hysteresis loop at room temperature.[4] It was also found experimentally that the Mn-substituted layer emits violet photoluminescence (382 nm) at 20 K by ultraviolet excitation, suggesting that the layer becomes a wide gap semiconductor.

After publication of aforementioned results, we have been trying to prepare $CdGeP_2$:Mn polycrystalline powder in order to get single-phase material. We have just elucidated that the polycrystalline material can also be prepared by solid-state reaction. This article describes the preparation and magnetic properties of the $CdGeP_2$:Mn single crystal layer and polycrystalline powders.

A single crystal of $CdGeP_2$ used as a starting material was grown at the Ioffe Institute by directional crystallization and had a shape of a flat–parallel crystal plate with size of 3×5 mm^2. 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 (MBE) chamber with the residual pressure of 1.4×10^{-8} Torr. A thin Mn layer of 30 nm in thickness was deposited from a Knudsen cell onto the $CdGeP_2$ single crystal in a MBE chamber, and then the thermal treatment was carried out at 500 °C for 30 min. The sample surface was monitored by reflection high-energy electron diffraction (RHEED), which showed a pattern characteristic of the (112) surface of the chalcopyrite lattice before deposition of Mn, and become diffused after the deposition. The crystalline pattern was recovered after the thermal treatment. Hereafter, we refer to this material as $CdGeP_2$:Mn single crystal layer.

On the other hand, polycrystalline powders of $CdGeP_2$:Mn were prepared by two-stage sintering technique as follows. In the first stage, $CdGeP_2$ polycrystalline powders were synthesized. Elements of Cd, Ge, and P were weighed to a stoichiometric composition ratio and were sealed into an evacuated silica ampoule together with a small amount of iodine to enhance the solid-state reaction. The ampoule was heated at 1000 °C for two weeks. The resulting ingot was ground to a powder and analyzed by the x-ray diffraction (XRD), which showed a pattern of the single chalcopyrite phase (see Fig. 1). The calculated XRD spectrum has excellent agreement with experimental data for the powder of the starting ternary compound $CdGeP_2$. In the second stage, the powder was put on an alumina boat together with the 20% molar ratio of Mn and was annealed in a furnace under the nitrogen flow of 3 l/min at 500 °C for 2 h.

[a]Electronic mail: satokats@cc.tuat.ac.jp
[b]Permanent address: Ioffe Physico-Technical Institute, St. Petersburg, Russia.

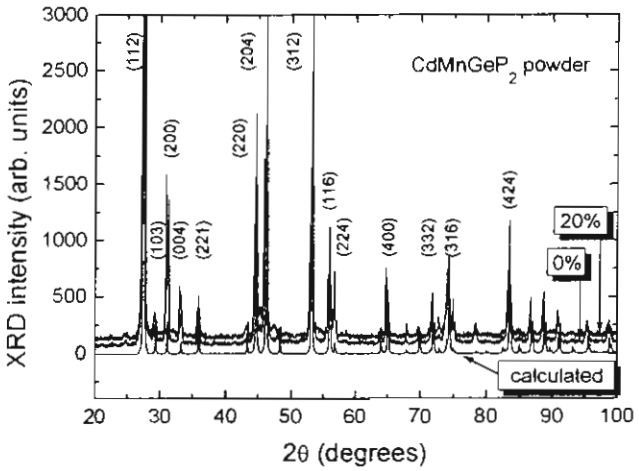

FIG. 1. XRD spectra of $CdMnGeP_2$ powders (Mn concentration is 0% and 20%) compared with the calculated XRD spectrum of pure $CdGeP_2$. Addition of Mn to the starting ternary compound induces a light shift of main peaks to higher angles 2θ.

The XRD measurements showed that crystal structures of both the single crystal layer[5] and the polycrystalline powder of $CdGeP_2$:Mn do not strongly differ from that of the host $CdGeP_2$; they all share the same chalcopyrite structure. Only a slight reduction of the lattice constants was observed in the Mn-substituted material. The obtained difference in the lattice constant was as small as <0.05 Å. The XRD pattern of the single crystal layer showed[5] the (112) diffraction line and three higher order lines (224), (336), and (448), while that of the polycrystalline sample exhibits a number of lines, all of which can be indexed to chalcopyrite lattice.

Special care was taken to examine the presence of any binary magnetic phases such as MnP (ferromagnetic, $T_C = 290.59$ K), Mn_2P (antiferromagnetic, $T_N = 103$ K), Mn_3P (antiferromagnetic, $T_N = 115$ K), Mn_3Ge (ferromagnetic, $T_N = 920$ K), and Mn_5Ge_3 (ferromagnetic, $T_C = 296$ K) accumulated in the literature.[6] We did not find any traces of these compounds in both samples. The energy dispersive x-ray (EDX) observation on the surface in the single crystal layer revealed that Mn/Cd ratio is as large as 0.53. This means about 1/3 of Cd has been substituted by Mn atom. The Mn/Cd ratio decreased rapidly toward the depth direction and the value becomes only 0.009 at 2.5 μm.

Figure 2 shows the measured data of magnetization versus magnetic field (M–H curve) in the $CdGeP_2$:Mn single crystal layer by the vibrating sample magnetometer technique at 300 K. Straight lines are for in-plane magnetization, and dots for perpendicular magnetization. The curves are composed of diamagnetic and ferromagnetic components. The former may be attributed to the diamagnetic contribution of the host semiconductor and the latter to the newly grown magnetic semiconductor phase. The ferromagnetic component shows a well-defined hysteresis loop with the saturation field Hs about 3 kOe and coercivity Hc of about 0.4 kOe. The saturation magnetization at room temperature was 3.5×10^{-4} emu. Assuming that the deposited Mn from the 30 nm thick layer on the 3×5 mm^2 surface area was completely incorporated into the host semiconductor, the magnetization

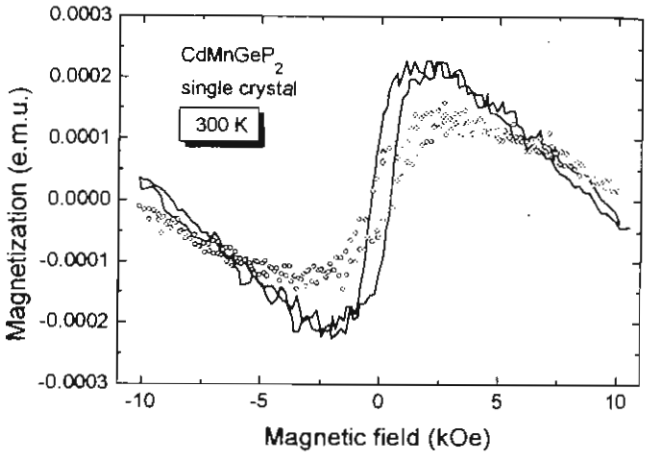

FIG. 2. M–H curves of $CdGeP_2$:Mn single crystal layer at $T = 300$ K in two orientations. Solid curves: in plane, open circles: perpendicular.

per atomic unit was evaluated as 0.96×10^{-20} emu/atom, from which the gS value was determined as 1.03 μ_B.

Figure 3 presents a plot of the magnetization as a function of temperature (M–T curve) measured at zero magnetic field for the single crystal sample $CdGeP_2$:Mn. The experimental data were fitted to an approximation of the molecular field theory. The best fit was obtained using the Brillouin function with $S = 1/2$. From the fitting procedure, the Curie temperature for $CdGeP_2$:Mn crystal was determined to be 320 K. Atomic force microscopy (AFM) and MFM measurements were carried out on the surface of the layer at room temperature.[4] In the AFM image, a textured structure consisting of small crystallites with the averaged size of 100 nm was observed, while in the MFM image, stripe domain patterns were obtained. The width of the stripe domains was about 1 μm, far larger than the size of the fine texture observed in the AFM image. This suggests the magnetization is not coming from individual fine texture but is uniformly distributing over the entire surface of the crystal.

Next, we show the results of the magnetic measurements on the polycrystalline powder of $CdGeP_2$:Mn. As shown in Fig. 4, the M–H curve at 123 K (wider sweep) exhibits well-

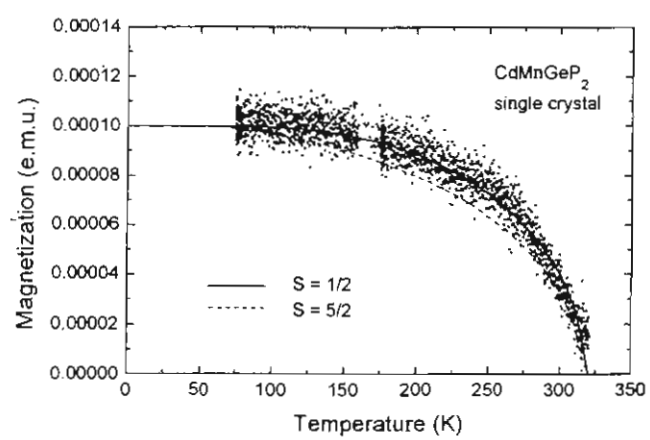

FIG. 3. M–T curve for the $CdGeP_2$:Mn single crystal layer taken at zero magnetic field.

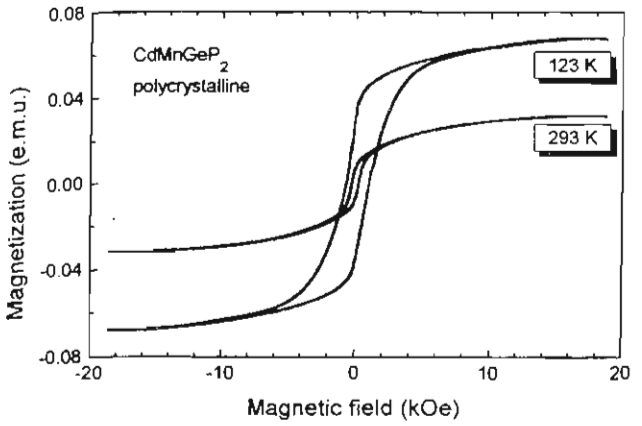

FIG. 4. M–H curves of $CdGeP_2$:Mn polycrystalline powder at two temperatures, T=123 K and 293 K.

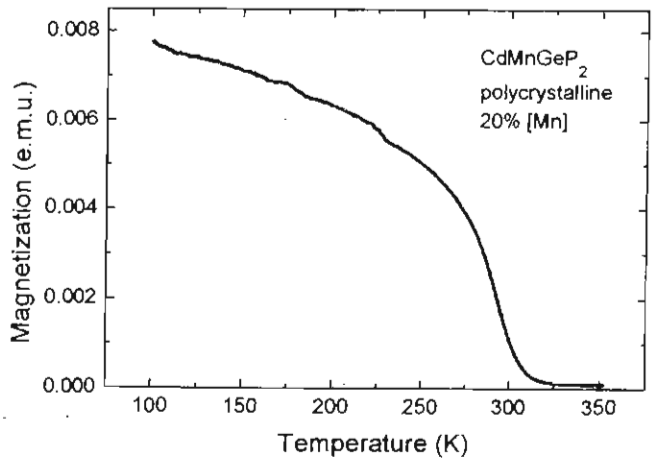

FIG. 5. M–T curve in the $CdGeP_2$:Mn polycrystalline powder taken at zero magnetic field.

defined hysteresis with Hc=0.84 kOe. The saturation field Hs is about 15 kOe. The diamagnetic component disappears in the powder, which means that the semiconductor was completely converted into the ferromagnetic phase. The M–H curve at room temperature (narrower sweep) shows a hysteresis loop with Hc=0.24 kOe and Hs=15 kOe. This indicates that the polycrystalline sample also exhibits ferromagnetism at room temperature. The M–T curve measured at zero magnetic field in the polycrystalline sample is shown in Fig. 5. The curve cannot be fit by a single Brillouin function curve, suggesting that the powder is not perfectly a single magnetic phase. Since the M–T curve of the polycrystalline powder shows a tail ranging from 300 to 320 K, accurate determination of Tc is difficult. We estimate Tc by extrapolation as 310 K, which is slightly lower than that of the single crystal layer. The finding that Curie temperatures of the two samples are not much different regardless of the diverse preparation methods suggests an existence of the ferromagnetic compound with a certain composition ratio.

Spectra of the polar magneto-optical Kerr ellipticity η_K were measured[4] on the surface of $CdGeP_2$:Mn single crystal layer under the applied field of $H=\pm 1$ T. The η_K has a distinct negative peak at 1.75 eV (T = 300 K) followed by a gradual decrease towards higher energies. The peak energy position coincides with the energy gap of $CdGeP_2$ crystal. Using the peak value of η_K the specific Faraday rotation is estimated as 5×10^4 degrees/cm, which is comparable to the Faraday rotation of Bi-substituted magnetic garnet. Details will be published elsewhere.[7,8]

In conclusion, room temperature ferromagnetism was revealed for the first time in the magnetic semiconductor $CdGeP_2$:Mn. The Tc was experimentally determined as 320 K for the single crystalline phase and 310 K for the polycrystalline powder. Calculation of the magnetic moment per Mn-ion gave the value of $gS=1.03\ \mu_B$. The Faraday rotation in $Cd_xMn_{1-x}GeP_2$ layer was estimated to be as large as 5×10^4 degrees/cm.

[1] D. D. Awschalom and R. K. Kawakami, Nature (London) **408**, 923 (2000).
[2] H. Ohno, D. Chiba, F. Matsukura, T. Omiya, E. Abe, T. Dietl, Y. Ohno, and K. Ohtani, Nature (London) **408**, 944 (2000).
[3] H. Ohno, J. Magn. Magn. Mater. **200**, 110 (1999).
[4] G. A. Medvedkin, T. Ishibashi, T. Nishi, K. Hayata, Y. Hasegawa, and K. Sato, Jpn. J. Appl. Phys., Part 2 **39**, L949 (2000).
[5] G. A. Medvedkin, T. Ishibashi, T. Nishi, and K. Sato, Semiconductors **35**, 291 (2001).
[6] O. Beckman and L. Lundgren, in *Handbook of Magnetic Materials*, edited by K. H. J. Buschow (North–Holland, Amsterdam, 1991), Vol. 6, p. 181.
[7] K. Sato, G. A. Medvedkin, K. Hayata, Y. Hasegawa, T. Nishi, R. Misawa, and T. Ishibashi, J. Magn. Soc. Jpn. **25** (2001) (to be published).
[8] G. A. Medvedkin, K. Hayata, Y. Hasegawa, T. Nishi, T. Ishibashi, and K. Sato, in *Proceedings of the International Conference on Basic Problems of Optics*, St. Petersburg, Russia, 17–19 Oct. 2000 (Publication Office of the Technical University of Fine Mechanics and Optics, St. Petersburg, Russia, to be published).