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New magnetic materials in $ZnGeP_2$-Mn chalcopyrite system

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Abstract

The growth of quaternary solid solutions in the $ZnGeP_2$-Mn quasi-binary system was studied. Single-crystal thin layers of $ZnGeP_2$:Mn with a basal crystal structure appurtenant to the chalcopyrite crystal class were grown for the first time. Ferromagnetic behavior of the $ZnGeP_2$:Mn compound was observed up to a temperature of 350 K. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Chalcopyrite crystals of $ZnGeP_2$ are of great interest for nonlinear optical applications because of their high figure of merit. Optical parametric oscillators and frequency converters for high-power mid-IR sources show an external efficiency as high as 35% and broad-band tuning in the range of $\Delta\lambda = 3.8-12\,\mu m$ in this material [1,2]. An additional degree of freedom under tuning by a magnetic field or crystal-chemical composition may be obtained in $ZnGeP_2$ single crystals or epitaxial layers by incorporating magnetic atoms into the chalcopyrite lattice. The recent discovery of ferromagnetism in the chalcopyrite semiconductor $CdGeP_2$:Mn [3,4] has made it possible to predict previously unknown magnetic properties in this chalcopyrite system. We prepared a $ZnGeP_2$:Mn single-crystal layer by deposition and diffusion of Mn on $ZnGeP_2$. We also prepared polycrystalline powder of $ZnGeP_2$:Mn by solid-state reaction.

2. Experimental procedure

Single crystals of $ZnGeP_2$ were grown by the vertical Bridgman technique at Siberian Physical

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Technical Institute. As starting material, polycrystalline $ZnGeP_2$ was prepared by the two-temperature dynamic method [5] using calculated thermodynamic data [6]. Single-crystal bulk ingots 28 mm in diameter and 150 mm in length were obtained. Single-crystal plates with the required crystallographic orientation were cut from the ingots. The samples show high-resistivity p-type conduction. Oriented single crystals of $ZnGeP_2$ {0 0 1} were polished and etched using the chemical mechanical polishing (CMP) technique. Mn was evaporated from a Knudsen cell and was deposited onto the crystal surface of these single crystals in a molecular beam epitaxy (MBE) chamber at a substrate temperature of 400°C for 30 min. During this process, the deposition and diffusion of Mn and the subsequent solid-state reaction were simultaneously undertaken. The process was monitored in situ using a reflection high-energy electron diffraction (RHEED) technique. The Mn-diffused single-crystalline layer of $ZnGeP_2$ was characterized accurately by X-ray diffraction (XRD) using the Rigaku RINT-RAPID system with glancing angle incidence of X-rays. Magnetization of the Mn-diffused layer was measured at Institute for Materials Research of Tohoku University, using a superconducting quantum interference device (SQUID) magnetometer.

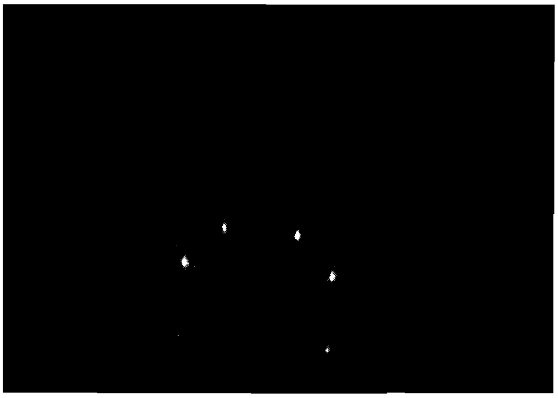
Polycrystalline $ZnGeP_2$:Mn powders were synthesized by a solid-state reaction at Tokyo University of Agriculture and Technology. A cylindrical furnace with a quartz reactor and a thermocontroller CHINO model KP were employed for the growth. The polycrystalline ternary compound of $ZnGeP_2$ was synthesized directly from constituent elements (5 N grains of Zn, 4 N grains of Ge and 5 N chunks of P). Polycrystalline $ZnGeP_2$ material obtained after this initial stage shows the chalcopyrite structure with an excess of Ge. In the second stage, a chemical reaction with Mn was carried out at 500°C for 2 h in N_2-flow to form $ZnGeP_2$-Mn solid solution. The XRD analysis was performed using a Rigaku RAD-IIC apparatus and the JCPDS database. The effect of magnetization was measured with a Toei vibrating sample magnetometer (VSM) in the temperature range of 80–350 K.

3. Results and discussion

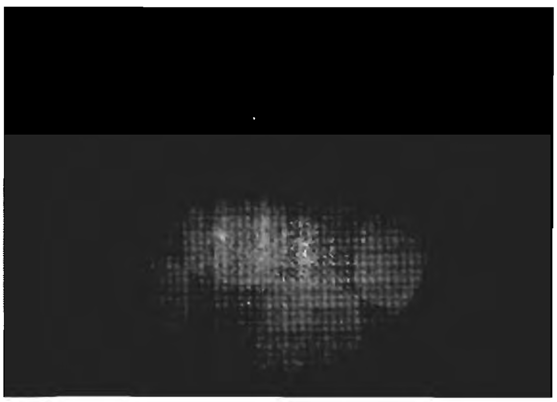
Fig. 1 illustrates RHEED patterns showing the $ZnGeP_2$ single-crystal surface (a) before, (b) during and (c) after the solid-phase chemical reaction with Mn. The RHEED pattern before deposition (Fig. 1(a)) shows a Laue spot with well-defined Kikuchi lines suggesting a high quality of the crystal surface. The pattern changes to a streaky image during Mn deposition as shown in Fig. 1(b) and to a spotty pattern indicating a roughened surface at the finishing stage shown in Fig. 1(c). The streaky pattern observed during deposition implies the appearance of flat terraces on the crystal surface during Mn-deposition, suggesting that the chalcopyrite phase is sustained even when the Mn covers the surface. We believe that the deposited Mn atoms diffuse into the lattice as soon as they reach the surface of the crystal, since a streak pattern never appeared when the substrate was kept at room temperature during deposition. The high-sensitivity XRD pattern of the Mn-diffused single-crystalline layer of $ZnGeP_2$ is shown in Fig. 2, in which a trace of the ring pattern of the secondary polycrystalline phase was scarcely observed.

Fig. 3 shows a magnetization curve of the Mn-diffused sample measured using a SQUID magnetometer at 350 K. The inset is a magnified plot showing the hysteresis loop, in which ferromagnetic behaviors were clearly observed, although the value of the saturation magnetization Ms was quite small. The value of Ms showed no observable change between 15 and 350 K, indicating that this material has a considerably high Curie temperature. We have thus succeeded in observing room-temperature ferromagnetism in the $ZnGeP_2$-Mn system, as well as in the $CdGeP_2$-Mn system. We believe that room-temperature ferromagnetism is a phenomenon common to all the Mn-diffused II–IV–V_2 semiconductors.

On the other hand, in the polycrystalline $ZnGeP_2$:Mn material with 20% Mn, a strong ferromagnetism at room temperature with a hysteresis loop was observed, from which the coercivity H_c and saturation field H_s were determined to be 0.22 and 1.6 kOe, respectively. The Curie temperature was determined to be 300 K



(a)



(b)

(c)

Fig. 1. Variation of the RHEED pattern during the process of Mn deposition on a $ZnGeP_2$ crystal, (a) before deposition of Mn, (b) during deposition of Mn, and (c) after deposition.

from the temperature dependence curve of magnetization. Although very weak, magnetization

Fig. 2. An XRD photograph of the Mn-diffused layer measured using the Rigaku RINT-RAPID system with glancing angle incidence of X-rays. (Spots can be associated with the chalcopyrite lattice.)

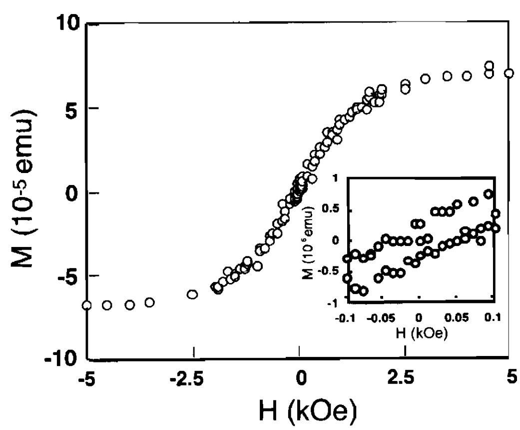


Fig. 3. Magnetization vs. magnetic field curve measured with SQUID magnetometer at 350 K. The inset shows a magnified plot indicating a hysteresis behavior.

still remained above 320 K. Fig. 4 shows an XRD pattern of the polycrystalline $ZnGeP_2$:Mn. We intended to perform Rietvelt analysis to determine the crystal structure and lattice parameters of $ZnGeP_2$:Mn. However, we failed to obtain single-phase powder samples, despite repeated efforts of synthesis. Although the dominant XRD peaks were assigned to the chalcopyrite phase (denoted 1–20), they were always accompanied by peaks ascribed to Ge and a few unknown lines. We carefully examined the sample for the presence of Mn-containing phases that are potential sources of magnetism, such as MnP (ferromagnet) and Ge_2Mn_3 (ferrimagnet) [7] by comparison with

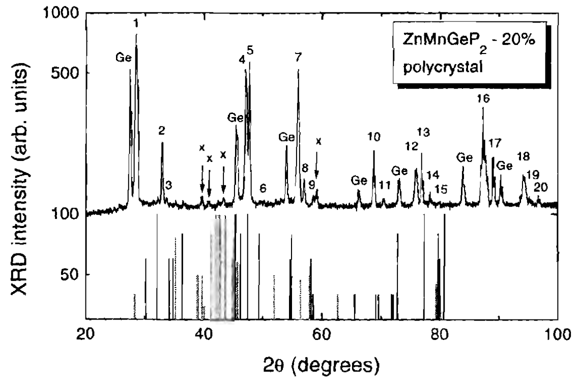


Fig. 4. An XRD pattern of the polycrystalline powder of Mn-diffused $ZnGeP_2$. Diffraction peaks 1–20 can be assigned to the chalcopyrite lattice, indicating that the dominant phase is chalcopyrite. Secondary phases: Ge (determined) and × (unidentified). In the lower part, column bars denote compilation of XRD peaks from JCPDS for MnP, Ge_2Mn_5 and Ge_2Mn_3 binary compounds.

JCPDS (1998) data (column bars in the lower part in Fig. 4), but they were not presenting compounds such as MnP, Mn_2P and MnP_4. Ge_2Mn_3, Ge_2Mn_5 (cards 24–446 and 35–1409), Ge_3Mn_5, Ge_5Mn_3, GeMn, $GeMn_{2.3}$, $GeMn_{3.4}$, $GeMn_2$ and $GeMn_3$ were also not found. Nevertheless, at this time we cannot completely rule out the formation of unknown ferromagnetic Mn-containing phases, since a few peaks denoted by × remain unidentified. Further investigation is necessary to determine the origin of the room-temperature ferromagnetism in polycrystalline powder.

4. Conclusion

New quaternary material in the $ZnGeP_2$-Mn chalcopyrite system was grown for the first time. The Mn-diffused layer on the single crystal of $ZnGeP_2$ shows the chalcopyrite crystal structure and a ferromagnetic magnetization curve up to 350 K, the highest temperature at which we conducted measurements. We believe that room temperature ferromagnetism is a common phenomenon among the Mn-diffused II–IV–V_2 semiconductors. This finding extends the potentiality of magnetic semiconductors for future application to spin electronics.

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