

Anomalous Hall effects and magneto-resistance in MnGeP₂ thin films

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Abstract: Field dependent magnetization experiments were performed for MnGeP₂ thin films on GaAs(100) substrate with a ferromagnetic transition near 325 K, which showed coercive fields of 3900, 1400 and 160 Oe at 5, 255 and 300 K, respectively. The effective coercive fields by the Hall measurements were 4900, 4300, 3000, 300 Oe at 5, 105, 205, 305 K, respectively, in relatively good agreements with those measured by field dependent magnetization experiments. Magnetoresistance and Hall measurements have displayed hysteric behaviors with respect to the external field sweep, which implies that the conducting carriers can be spin polarized by the external magnetic field.

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I. Introduction

Through the last two decades, the field of magneto-electronics, currently called spintronics, has grown steadily, driven by the discovery of such spin-dependent phenomena as giant magneto-resistance and the industrially-successful magnetoresistive (MR) sensor with a spin-valve structure [1]. The development of spin polarized carrier transport in semiconductors may lead to novel spin dependent electronic devices. Historically, the semiconductors utilized in devices have been nonmagnetic. Earlier studies on semiconductors showed that II-VI semiconductors with a low concentration of magnetic impurities displayed magnetic behavior only at low temperatures [2]. The discovery of ferromagnetism in Mn-doped GaAs with a relatively high temperature (~100 K) [3,4] attracted much attention since it offered an alternate way to overcome the rapid spin polarization loss during spin injection observed between nonmagnetic semiconductors and ferromagnetic metals [5,6]. Spin injection from a ferromagnetic semiconductor to a lattice and Fermi-level matched nonmagnetic semiconductor should significantly reduce the spin-flip scattering rate.

The tetragonal chalcopyrite II-IV-V₂ structure is very similar to the tetrahedrally-coordinated zincblende III-V structure. It was discovered that when Mn is doped into some well known nonmagnetic II-IV-V₂ chalcopyrites, such as CdGeP₂ [7] and ZnSnAs₂ [8], ferromagnetic (FM) ordering occurs above room-temperature, with nominal T_C values of 320, 329 and 312 K, respectively. These ferromagnetic semiconducting materials, with high T_C, have the potential to advance spintronic devices if their magnetizations are associated large spin polarized carrier densities, and researches have been done on various ferromagnetic chalcopyrites materials [9-15].

In this letter, the magnetic and electrical transport properties of chalcopyrite semiconducting films of MnGeP₂, with room-temperature ferromagnetism will be presented. The advantage of this material over some other diluted magnetic semiconductors (DMS), such as Ga_{1-x}Mn_xAs and (Zn_{1-x}Mn_x)GeP₂, is that in this stoichiometric semiconductor, the magnetic 2⁺ Mn ions occupy all the group II sites (25% of the lattice sites), resulting in a larger magnetization than for DMS.

Thin films of MnGeP₂ were deposited on GaAs (001) (a = 5.65 Å) substrates with a molecular beam epitaxy (MBE) system. The deposition rate was ~ 0.5 Å/s. The substrate temperature during the growth was 350°C. The lattice constants for MnGeP₂ are a = 5.655 Å and c = 11.269 Å in bulk sample [9]. Scanning electron microscope images have shown that the layers (less than 500 Å) are flat and smooth. Energy dispersive x-ray spectroscopy (EDX) measurements show that the films have suitable compositions of Mn, Ge and P to make the chalcopyrite structure. More detailed information of the deposition of MnGeP₂ thin films is described elsewhere [16].

The magnetic properties of the films were investigated using a Quantum Design SQUID magnetometer. The temperature-dependent magnetization (M) of a MnGeP₂ film in a 250 Oe magnetic field (H) between 5K and 400 K is shown in Fig. 1. The sample shows a magnetic transition at near 325 K. Temperature-dependent electrical resistance data in zero magnetic field are shown in the inset of Fig. 1. The resistance of the film increases with temperature up to around 320 K and then saturates. The temperature 320 K, at which a distinct slope change occurs, corresponds to the ferromagnetic (FM)-paramagnetic (PM) transition temperature observed in the temperature-dependent magnetization measurement. A change in the spin-flip scattering rates between

the FM and PM regions presumably lead this resistance change at the phase transition. The resistivities at 5 and 300 K are 0.10 and 0.28 mΩ cm, respectively.

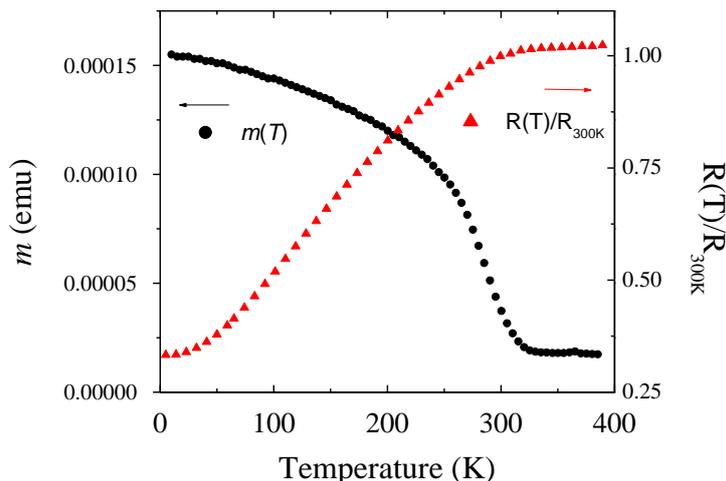


Fig. 1 Temperature dependent magnetization (black circle) in a 500 Oe magnetic field of a 170 Å MnGeP₂ film grown on a GaAs (001). Temperature dependent electrical resistance (red triangle) of a 340 Å MnGeP₂ film on GaAs (001) in zero magnetic field is shown in the same plot.

Magnetic field dependent magnetization (*M-H*) curves measured at 300 K indicate that at room-temperature and below, the film is ferromagnetic as shown in Fig. 2, so that the transition at near 325 K is a FM-PM transition. Note that the GaAs substrate is diamagnetic, which is removed in Fig. 2. The coercive fields of the MnGeP₂ film at 5 and 300 K are 3900 and 160 Oe, respectively. The magnetic moment per Mn atom at 5 K for the MnGeP₂ film obtained from the saturation magnetizations is 2.4 μ_B.

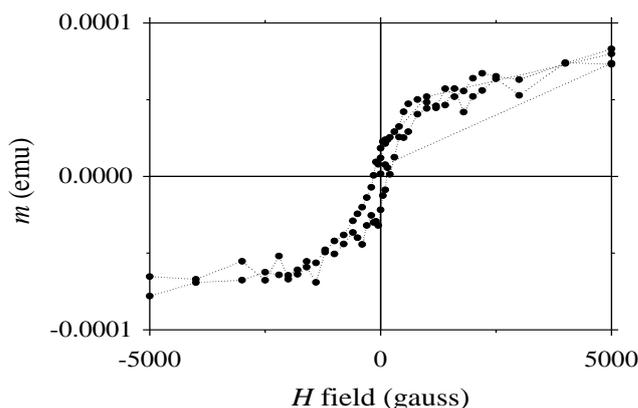


Fig. 2 Field dependent magnetization (*M-H*) curves from a 170 Å MnGeP₂ film at 300 K.

Field dependent Hall resistances have been measured at various temperatures, as shown in Fig. 3. In the measured 340 Å thick patterned MnGeP₂ film sample, the anomalous Hall effect has been observed apparently at temperatures below the FM-PM transition temperature, indicating the presence of spin polarized carriers in MnGeP₂. At 355 K, above the transition temperature, the curve is linear with respect to magnetic field, as expected for the ordinary Hall effect. At that temperature, the carriers have been found p-type and the effective carrier density is over 10²⁰ cm⁻³. This value must be changed if there occurs superparamagnetism in the sample at this temperature. Hysteresis in the field dependent Hall resistance curves is seen in the figure. When the magnetic field increases (decreases) between -1.5 and 1.5 T, the slope change occurs at positive (negative) magnetic field. The zero-anomalous-Hall-resistance fields in the curves, change in magnetic fields resulting in anomalous Hall resistance zero with the applied magnetic field sweeping direction, which are expected to be similar to the coercive field (so, is called effective coercive fields), are calculated and shown in Fig. 4. They vary from 4900 to 300 as the temperature changes from 5 to 305 K. The anomalous part of the

Hall resistivity has the form $4\pi R_s^\gamma M$, where R_s is sheet resistance and γ is an exponent [17]. In the film studied in this experiment, the exponent has been found to be very close to 2, which implies the transport of the film is governed by a “side-jump” mechanism and that the scattering is proportional to the impurity concentration [18].

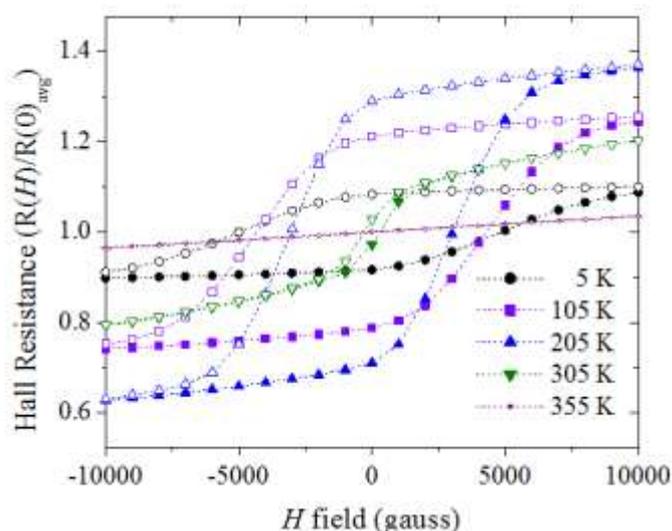


Fig. 3 Anomalous Hall resistances of a 340 Å p-type MnGeP₂ film at 5, 105, 205 and 305 K, respectively. Hall resistance of the film measured at 355 K shows linear behavior with respect to the H field.

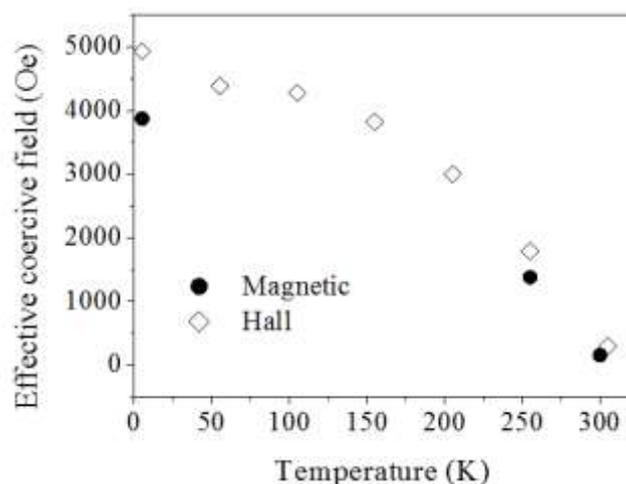


Fig. 4 Effective coercive fields of a 340 Å p-type MnGeP₂ film, which is the difference between positive (sweep up) and negative (sweep down) zero-anomalous-Hall-resistance fields (ZF) are shown. Coercive fields from M - H curves are also shown for comparison.

Magnetic field dependent resistance measurements were performed at 5 and 300 K. The resistance change in magnetic fields up to 5 T, at both 5 and 300 K, was found less than 2%. Figure 5 shows hysteresis in magnetoresistance of the film in low magnetic fields. Hysteresis is apparent in the data at 5 and 255 K. At 305 K, the difference in the peak position in the magnetoresistance curve between the field sweep up and down measurements is seen. No hysteresis has been seen at 355 K above the transition temperature. This provides important evidence that the carriers in the film are spin polarized [17]. When a small magnetic field is applied anti-parallel to the magnetization direction of the sample, two peaks are observed, due to the scattering. The carrier type in MnGeP₂ films is observed to be p-type, with carrier densities on the order of 10^{20} cm^{-3} above room temperature, as determined from Hall measurements. It is well known that in II-IV-V₂ chalcopyrites, there are various native defects such as group II and V vacancies and antisite defects with densities up to 10^{19} cm^{-3} [19,20]. Native point defects such as cation Mn and Ge vacancies and/or the anti-site defect Mn_{Ge} may result in

hole carriers in MnGeP₂ films. A MnGeP₂ film was deposited on an n-type GaAs(100) substrate and the current-voltage (I-V) characteristics measured. A typical p-n diode type I-V curve is observed for the MnGeP₂/n-GaAs system, indicating that the MnGeP₂ film layer is p-type.

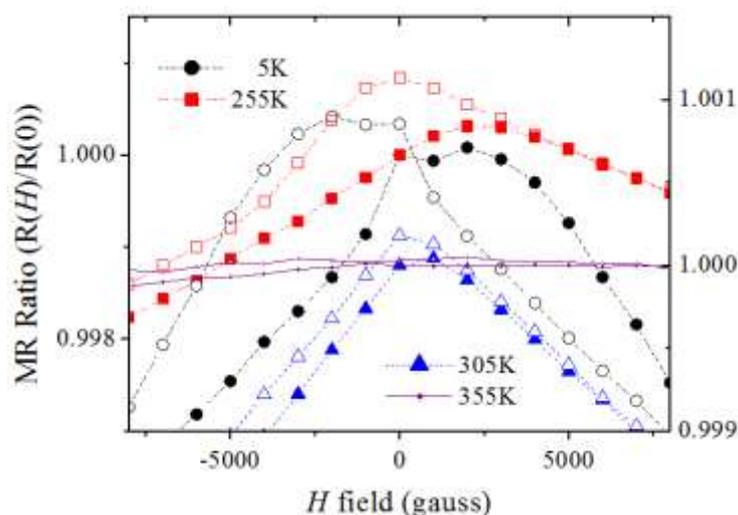


Fig. 5 Hysteresis in the magnetoresistance of the film at 5, 255 and 305 K, respectively; magnetoresistance data at 355 K are plotted for comparison. Data at 305 and 355 K are plotted corresponding to the scale of the right axis for clear discernment of the data points.

In conclusion, MnGeP₂ films have been synthesized. The films display room-temperature ferromagnetism and a high magnetic moment of 2.4 μ_B per Mn. We have observed anomalies in magnetic field dependent transport of the carriers, presumably due to spin polarization. The results of the present investigation suggest that chalcopyrite MnGeP₂ films are potential candidate elements for room-temperature spintronic devices.

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