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Growth and Magnetic properties of $MnGeP_2$ thin films

Yunki Kim*, J. B. Ketterson
Department of Electrical and Biological Physics, Kwangwoon University, Seoul 01897, Republic of Korea
Department of Physics & Astronomy, Northwestern University, Evanston, IL 60208, USA

Abstract: *We have successfully grown $MnGeP_2$ thin films on GaAs (100) substrate. A ferromagnetic transition near 320 K has been observed by temperature dependent magnetization and resistance measurements. Field dependent magnetization experiments have shown that the coercive fields at 5, 250, and 300 K are 3870, 1380 and 155 Oe, respectively. Magnetoresistance and Hall measurements have displayed that hole conduction is dominant in $MnGeP_2$.*

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I. Introduction

Earlier reports on II-VI semiconductors with a low concentration of magnetic impurities showed magnetic behavior only at very low temperatures [1]. The observation of ferromagnetism in Mn-doped GaAs attracted much attention since it displayed a relatively high transition temperature (~100 K) [2,3], suggesting a solution to an issue of the rapid spin polarization loss via scattering at the interface due to the Fermi level mismatch during the spin injection observed between nonmagnetic semiconductors and ferromagnetic metals [4,5] by using the ferromagnetic semiconductors in place of ferromagnetic metals. The fabrication of a single electronic device can be accomplished commercially available with spin dependent function such as magnetoresistive (MR) sensor as well as utilizing charge of electrons by allowing spin polarized carriers transport in semiconductors.

Tetragonal chalcopyrites (II-IV-V_2) have very similar structure to the tetrahedrally-coordinated zinc-blendes (III-V). This class of materials is important for various nonlinear optical applications since the tetragonal structure allows phase matching between beams having different wavelengths [6,7]. The observation of room-temperature ferromagnetism in Mn doped II-IV-V_2 semiconducting chalcopyrites, such as $CdGeP_2$, $ZnGeP_2$, and $ZnSnAs_2$ [8,9], with nominal ferromagnetic transition temperature T_C values of 320, 310 and 330 K, respectively, have leaded a more researches on various ferromagnetic chalcopyrites materials [10-17].

In this paper, the successful growth of chalcopyrite semiconducting films of $MnGeP_2$, with room-temperature ferromagnetism will be presented. And the magnetic and transport properties of the $MnGeP_2$ films and alloy films of $MnGeP_2$ and Ge are to be given. $MnGeP_2$ has a apparent advantage over diluted magnetic semiconductors (DMS), such as Mn doped $MnGeP_2$, $(Zn_{1-x}Mn_x)GeP_2$. In $MnGeP_2$, the magnetic impurity Mn^{2+} occupies the group II site (25% of the whole lattice sites), resulting in a larger magnetization value than in DMS. $MnGeP_2$ thin films were grown on GaAs (001) substrates using a molecular beam epitaxy (MBE) system. The deposition rate was 0.3-0.6 Å/s. The substrates were heated to 650 °C with an As flux to remove surface oxide of GaAs substrate, followed by the deposition of GaAs buffer layer (typically around 100 Å) to obtain smooth surface of the substrate. A streaky reflection high energy electron diffraction (RHHED) pattern after the clean and smooth surface of GaAs is reached is shown in Fig. 1(a). During the deposition, the substrate temperature was maintained at 350 °C. A RHHED pattern after a 170 Å thick film deposition is shown in Fig. 1(b), which implies a reconstructed surface structure of the film. The mismatch in the lattice constants between $MnGeP_2$ (a = 5.655 Å and c = 11.269 Å [10]) and GaAs (a = 5.65 Å) is less than 0.5 %; hence we could not resolved the film peaks from the GaAs substrate peaks in θ-2θ diffraction (XRD) measurements for our thin $MnGeP_2$ thin layers. The thickness of the films was 150-400 Å, confirmed by low angle x-ray reflectivity measurements. The film layers (less than 500 Å) were confirmed flat and smooth by scanning electron microscope images. The compositions of Mn, Ge and P were analyzed by energy dispersive x-ray spectroscopy (EDX) measurements.

Magnetic properties of the grown $MnGeP_2$ films were measured using a Quantum Design SQUID magnetometer. The temperature-dependent magnetization (*M-T*) curve of a $MnGeP_2$ film in a 1000 Oe magnetic field between 5K and 400 K is shown in Fig. 2. The measured magnetization curve do not show any antiferromagnetic behavior which is reported in $MnGeP_2$ bulk samples [10]. The sample shows a magnetic transition at around 320 K. Note that the GaAs substrate is diamagnetic, which is the reason a diamagnetic behavior is shown above the transition temperature. Magnetization (*M*) measurements with respect to the external field (*H*) have been performed and shows that the film is ferromagnetic below the magnetic transition temperature as shown in Fig. 3, so that the transition at or above 320 K is a ferromagnetic-paramagnetic (FM-

PM) transition. Note that the diamagnetic behavior of the substrate GaAs is included in the magnetization data. The coercive fields of the $MnGeP_2$ film at 5 and 300 K are 3870 and 155 Oe, respectively. The magnetic moment per Mn atom in the $MnGeP_2$ film has been calculated to be 2.4 μ_B from the saturation magnetization data at 5 K.

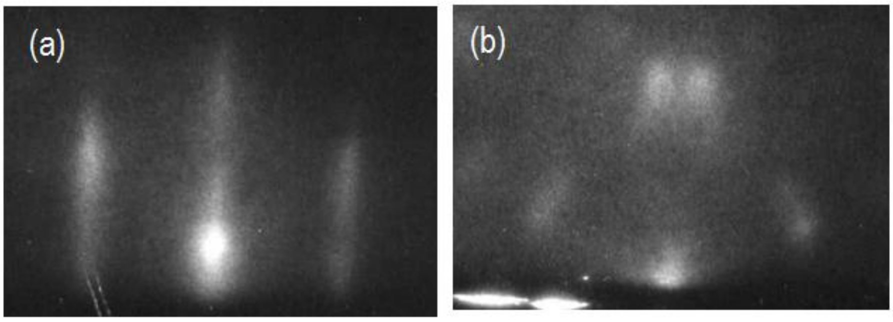

FIG. 1:(a) A RHEED pattern image of GaAs(100) substrate before the $MnGeP_2$ thin film (b) after the deposition of a $MnGeP_2$ thin film.

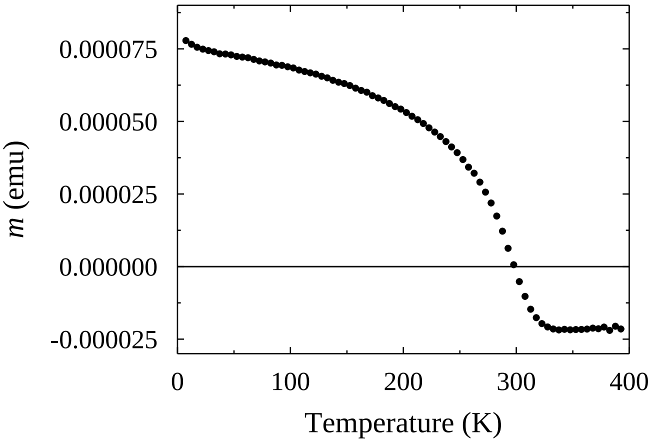

FIG. 2: Temperature dependent magnetization (*M*) in a 1000 Oe magnetic field of a 170 Å $MnGeP_2$ film grown on a GaAs (001). The diamagnetic behaviors shown above the transition temperature come from the GaAs substrate.

Electrical resistance data from 5 K to 400 K in zero magnetic field are shown in Fig. 4. The resistance of the $MnGeP_2$ film increases with temperature up to around 320 K and then saturates. The resistance increase with temperature often indicates that the sample has relatively large number of mobile carriers or that it has very small bandgap. The carrier densities of the film by a Hall measurement above the transition temperature was over 10^{20} cm^{-3}. A distinct slope change occurs at near 320 K, which corresponds to the FM- PM transition temperature observed in the temperature-dependent magnetization measurements. Spin-flip scattering rates could be different between the FM and PM regions, which may result in the change of slopes in resistance. Electrical resistance measurement on another sample which is the alloy film of $MnGeP_2$ and Ge has been performed. The lattice constant of Ge is a = 5.658 Å, which is very close to those of GaAs and $MnGeP_2$, which may lead that they are to be alloyed well with each other. The composition of Mn, Ge and P of the alloy film has been measured by EDX to be 0.15, 1 and 0.3, respectively. The measured resistance of the alloy film decreases as temperature increases as shown in Fig. 4, which is a indication that this is a semiconductor and that there are not enough number of magnetic atoms in adjacent sites to effects even possibly by percolation on the resistance.

The resistance in magnetic fields up to 5 T, at both 5 and 300 K, has been performed and showed that the change was less than 2%. Hall resistances have been measured at various temperatures, as shown in Fig. 6(a) for the $MnGeP_2$ film and in Fig. 6(b) for the $MnGeP_2$ and Ge alloy film. In the $MnGeP_2$ film sample, the anomalous Hall effect has been observed at all measured temperatures below the ferromagnetic transition temperature, implying the presence of spin polarized carriers in the sample. For comparison, only Hall measurement data at 5, 55 and 305 K are shown in the figure. This provides an evidence that the carriers in the film are spin polarized. At 355 K, no anomalous effects are observed. The carrier densities have been calculated to be 6×10^{20} cm^{-3} and the major mobile carriers are found to be p-type at the temperature. This value must be changed if there occurs superparamagnetism in the sample at this temperature. It has been reported that there are various native defects in II-IV-V$_2$ chalcopyrites such as group II and V vacancies and antisite defects with densities up to 10^{19} cm^{-3} [6,7]. The anti-site defect Mn$_{Ge}$ and cation Mn and Ge vacancies may lead to make hole carriers in MnGeP$_2$ thin films. Hysteresis in the Hall resistance curves for the MnGeP$_2$ film is apparent as shown in the figure. There are two field points according to the magnetic filed sweeping direction where the anomalous Hall resistance is zero, the difference of which is expected to be similar to the coercive field in the magnetization measurement. The difference between two field points, so-called effective coercive field, vary from 4900, 4300 to 300 Oe as the temperature varies from 5, 55 to 305 K. For the Ge and MnGeP$_2$ alloy film, the same Hall measurement has been performed. The anomalous Hall effect has been observed at 10 and 55 K, and no anomalous effect has been found at or above 105 K. Apparent hysteresis has been observed only at 10 K, where the effective coercive field is around 3000 Oe and comparable but smaller than the values of the pure MnGeP$_2$ film at 5 and 55 K. This result may be attributed to the low spin polarized carriers due to low magnetic atom density in the alloy film than the pure MnGeP$_2$ film [18].

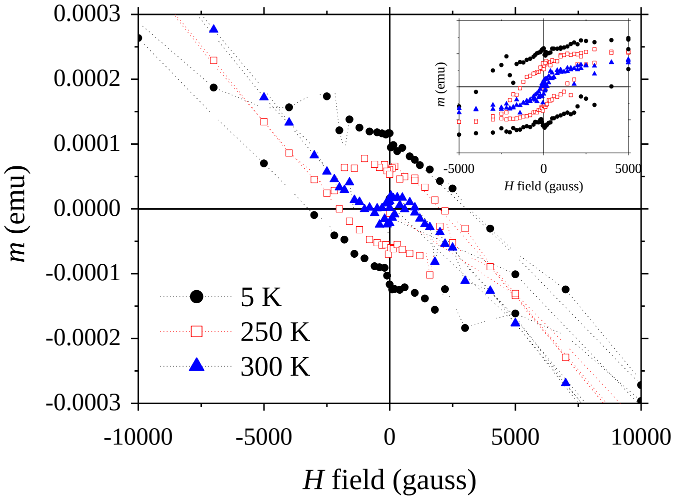

FIG. 3: M-H curves for the MnGeP$_2$ film and the GaAs substrate at 5, 250, and 300 K. The inset shows *M-H* curves only for the MnGeP$_2$ film by removing the diamagnetic behavior due to the substrate.

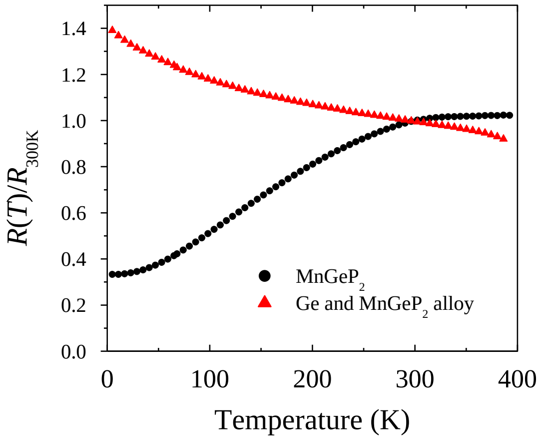

FIG. 4: Temperature dependent resistivities of a MnGeP$_2$ film (black solid circle) and of a Ge and MnGeP$_2$ alloy film (red solid triangle) from 5 to 400 K in zero magnetic field.

In conclusion, MnGeP$_2$ thin films were successively grown. The MnGeP$_2$ films show room-temperature (above 320 K) ferromagnetism and a magnetic moment of 2.4 μ_B per Mn. We have observed anomalous Hall effects, which implies the spin polarized carriers transport. The chalcopyrite MnGeP$_2$ films display hole-type conduction. The properties of MnGeP$_2$ films show that they can be used as key materials for spintronic applications.

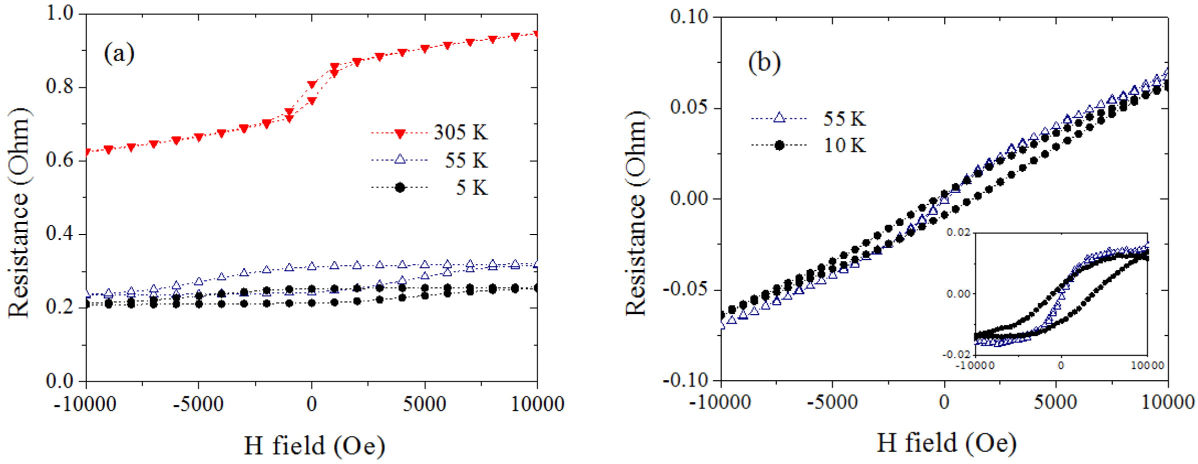

FIG. 5: (a) Hall resistances of a MnGeP$_2$ film with respect to the magnetic fields at 5, 55, 305 K and (b) Hall resistances of a Ge and MnGeP$_2$ alloy film at 10 and 55 K.

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