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Magneto-transport properties of $MnGeP_2$ and $MnGeAs_2$ films

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ABSTRACT
$MnGeAs_2$ and $MnGeP_2$ thin films were deposited on GaAs and Si substrates. For these film samples, room-temperature ferromagnetism was observed from magnetization and resistance measurements and verified from hysteresis in magnetization measurements. Hysteresis as well as anomalous behavior in Hall effect measurements was found in the deposited $MnGeAs_2$ and $MnGeP_2$ films, implying spin polarization of the mobile carriers in the films. The Hall resistance measurements above the ferromagnetic transition temperature showed that the carriers are n-type in $MnGeAs_2$ and p-type in $MnGeP_2$.
Keywords: $MnGeAs_2$, $MnGeP_2$, room-temperature ferromagnetism, anomalous Hall effect, MR hysteresis

I. INTRODUCTION

For the development of devices utilizing the properties of spins as well as charges of carriers in various materials, spin polarized carrier transport is essential [1]. Currently commercially available spin dependent devices such as magneto-resistive (MR) head and magnetic tunnel junction (MTJ) use the spin transport of carriers. In the last decades, technological advances in the field of magneto-electronics has grown rapidly, motivated by the findings of various spin-dependent phenomena such as giant magneto-resistance (GMR) and by the invention of spin-valve structure which is industrially successful as a magnetic sensor in hard disk drive systems [2]. Currently available materials used in the spin-dependent devices are mostly ferromagnetic metals, while to reduce the size and enhance the performance of spin dependent devices, fully established processing technology in semiconductor industry as well as some useful properties of semiconductors may be necessary. However, it is not efficient to flow spin polarized current through the semiconductors from ferromagnetic metals due to large and rapid spin polarization loss during spin injection between nonmagnetic semiconductors and ferromagnetic metals [3,4]. Incidence of diluted magnetic semiconductors (DMS), such as GaAs doped with Mn [5,6] attracted much attention since they can give one of the alternate ways to overcome the rapid spin polarization loss Spin injection from a ferromagnetic semiconductor to a lattice and Fermi-level matched nonmagnetic semiconductor should significantly reduce the spin-flip scattering rate.

DMS is a useful strategy to achieve control over the spin degree of freedom [7], an extra variable we can utilize, substituting magnetically active transition metal ions such as Mn, Ni, Fe, Cr, and Co into non-magnetic semiconductor hosts. Various DMS including, IV [8,9], III-V [10,11], and II-VI [12] semiconductors have been reported. In these classes of semiconductors, the low solubility of magnetic impurity ions in host semiconductors can limit the possibility to acquire high magnetic moments and high transition temperatures. Chalcopyrites (II-IV-V_2), acknowledged as promising for solar cells, detectors, and nonlinear optical devices [13], with a similar structure and close lattice constants with zinc-blende (III-V) materials, drew much attention as a promising candidate replacing DMS since the magnetic 2^+ ions can occupy all the group II sites (25% of the lattice sites) in a chalcopyrite structure. Mn-doped chalcopyrites such as $CdGeP_2$ [14], $ZnSnAs_2$ [15] and $ZnGeP_2$ [16] were reported to have ferromagnetic (FM) orderings near or above room temperature. These ferromagnetic semiconducting chalcopyrites, with high transition temperatures and similar crystal and electronic structures to the popularly used zinc-blende semiconductors, have potential to improve the performance of spintronic devices. Here we report the magnetic and magneto-transport properties of chalcopyrite films of $MnGeAs_2$ and $MnGeP_2$ on GaAs and Si substrates, with room-temperature ferromagnetism. And the spin-dependent I-V characteristics of a p-i-n diode structure with the $MnGeAs_2$ and $MnGeP_2$ multi-layers.

II. EXPERIMENT

Thin layers of $MnGeAs_2$ and $MnGeP_2$ were grown on GaAs(100) and Si(100) substrates with a molecular beam epitaxy (MBE) system. GaAs and Si substrates were heated before the film deposition upto 650 °C substrate to remove surface oxide at the surface and to obtain smooth surface. For GaAs substrates, an arsenic flux was maintained during the pre-heating process to compensate As out-gassing from the GaAs substrates. Then thin GaAs buffer layer deposition (50-150 Å) was followed, if necessary. The deposition rate was maintained to be around 0.5 Å/s. The substrate temperature during the growth was 350 °C when GaAs was used as a substrate. MnGeAs films on Si substrate were deposited at a higher substrate temperature of 500-700 °C. To assure the correct final composition the flux of As was maintained at about 20 times that of the manganese and germanium. To monitor crystal orientation and mode of growth of the deposited film, reflection high-energy electron diffraction (RHEED) was used. The thickness of the thin layers was measured in-situ using a quartz thickness monitor system.

III. RESULTS AND DISCUSSION

As shown in Fig.'s 1(a), (b) and (c), streaky RHEED patterns before and during the film deposition at 20 and 500 seconds were observed for a GaAs substrate and for a $MnGeP_2$ film on GaAs. The patterns were becoming weaker during the deposition as shown in the figures, implying that as the deposition proceeds, the surface of the deposited film becomes coarse. $MnGeAs_2$ films were grown on GaAs(100) and Si(100) substrates. The substrate temperatures were 350 °C for GaAs and 500-700 °C for Si. RHEED patterns for the films deposited on GaAs were streaky as shown in Fig.'s 1(d) throughout the deposition for over 1000 seconds. RHEED patterns taken from a Si substrate after pre-heating and a $MnGeAs_2$ film Si(100) were streaky, as shown in Fig.'s 1(e) and (f) .

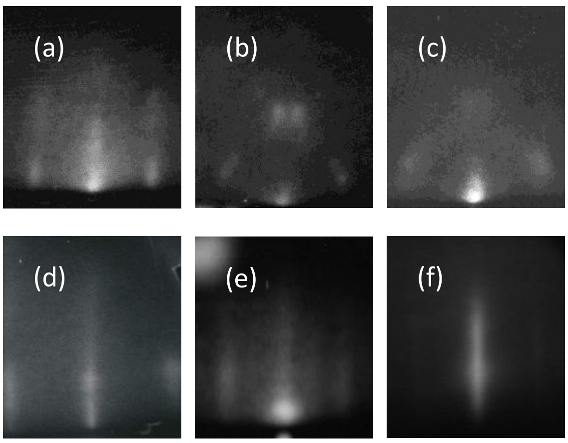

Fig. 1 RHEED images of (a) GaAs(100) substrate before the deposition and those of a $MnGeP_2$ film on GaAs(100) during the deposition in (b) 20 and (c) 500 seconds. (d) A RHEED image of a $MnGeAs_2$ film on GaAs(100) during the deposition and those of (e) Si(111) substrate before the deposition and of (f) a $MnGeAs_2$ film on Si(100) during the deposition.

$MnGeAs_2$ has lattice constants of a = 5.782 and c = 11.323 Å in bulk, while those for $MnGeAs_2$ are a = 5.655 and c = 11.269 Å [17]. The lattice mismatch between $MnGeAs_2$ and GaAs (a = 5.65315 Å) is 2.28% for a (0.15% for c/2) (with Si (a = 5.4307 Å), 6.47% (4.25%)) and that between $MnGeP_2$ and GaAs is 0.0327% for a (0.330% for c/2) (with Si, 4.13% (3.75%)). Hence for our very thin $MnGeAs_2$ and $MnGeAs_2$ layers, we could not resolve the film peaks from the GaAs substrate peaks in x-ray θ-2θ diffraction (XRD) measurements, as shown in Fig. 2. XRD measurements on a $MnGeAs_2$ film on Si(100) substrates with a considerable lattice mismatch with the film showed a couple of XRD films peaks as shown in the figure. The peaks could be identified as (200) and (400) from a chalcopyrite ordering and other peaks from the film layers were not found on a log scale plot. The (004) and (008) peaks, which are expected in a crystal with a chalcopyrite ordering were not found, suggesting that the grains on Si(100) do not have a chalcopyrite structure but a mixed (zinc-blend) structure. Scanning electron microscope (SEM) was used to characterize the surface morphology of the grown films. $MnGeAs_2$ grains look to be distributed randomly over the whole area and not relatively smooth. The composition of Mn, Ge, and As (or P) for the film samples were determined by energy dispersive x-ray spectroscopy (EDX) measurements, as summarized in Table 1. From the EDX measurements, the composition of Mn, Ge, and As deviates from stoichiometric value of (1: 1: 2).

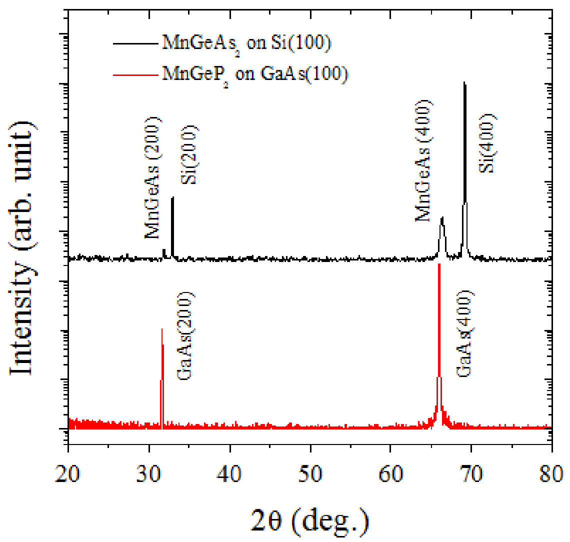

Fig. 2 θ-2θ XRD patterns of a $MnGeAs_2$ film on Si(100) substrate deposited at substrate temperature of 600 °C and of a $MnGeP_2$ film on GaAs(100) at temperature of 350 °C, on a logarithmic scale.

Table 1 Compositions of Mn, Ge, and As or P of several $MnGeAs_2$ and $MnGeP_2$ films from EDX measurements. (Note that the gallium or arsenic composition of a film on GaAs substrate cannot be determined.)

Samples (substrate and growth temperature (^oC))	Composition		
	Mn	Ge	As or P
$MnGeAs_2$ (Si(100), 600)	0.72	1	2.02
$MnGeAs_2$ (GaAs(100), 350)	1.23.	1	
$MnGeP_2$ (GaAs(100), 350)	1.64	1	1.74

The magnetizations of the film samples were measured using a SQUID (Quantum Design) magnetometer. Magnetization (*M*) measurements on $MnGeAs_2$ and $MnGeP_2$ film samples were performed in a small (1000 Oe) external magnetic field (*H*) from 5 to 400 K, as shown in Fig. 3. All the samples display magnetic transitions above room temperature, around 320 and 350 K. Note that the negative magnetization values above the transition temperature for the film samples on GaAs come from the GaAs substrate which is diamagnetic. Temperature dependent electrical resistance measurements from 5 to 400 K in zero magnetic field show that the $MnGeAs_2$ and $MnGeP_2$ films on GaAs have a metallic behavior in resistance which increases with temperature up to the transition temperature observed in the magnetization measurement but above the temperature saturates. This distinct change in the resistance curve seems to be caused by spin-flip scattering rate between ferromagnetic (FM) and paramagnetic (PM) temperature regions, which leads the slope change in resistance at the transition temperature. Field dependent magnetization measurements were also performed for the film samples at 5 and 300 K (and 250 K for the films on GaAs). The hysteric ferromagnetic *M-H* curves were observed at room-temperature (300 K) and below (5 K or 250 K), suggesting that the transitions around 320 and 350 K are FM-PM transition. Among them, *M-H* curves for the films at 5 K and 300 K are shown in Fig's 4(a) and (b). The coercive fields of the $MnGeAs_2$ and $MnGeP_2$ films are summarized in Table 2. The magnetic moment per Mn atom at 5 K for the $MnGeAs_2$ and the $MnGeP_2$ films on GaAs were obtained to be 3.4 μ_B and 2.4 $\mu_{B,}$ respectively, from the saturation magnetization value at 5 K, which is in good agreement with the bulk value [17].

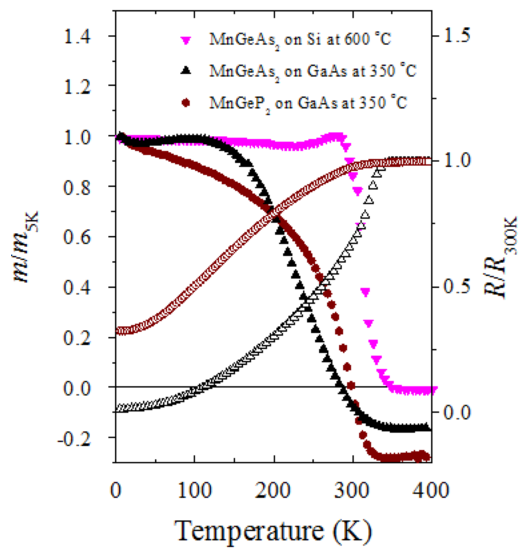

Fig. 3 Magnetization of $MnGeAs_2$ films on GaAs and Si and of a $MnGeP_2$ film on GaAs, normalized with their value at 5 K, scaled on left axis. And, electrical resistance of a $MnGeAs_2$ and a $MnGeP_2$ film on GaAs, normalized with their value at 300 K, scaled on right axis.

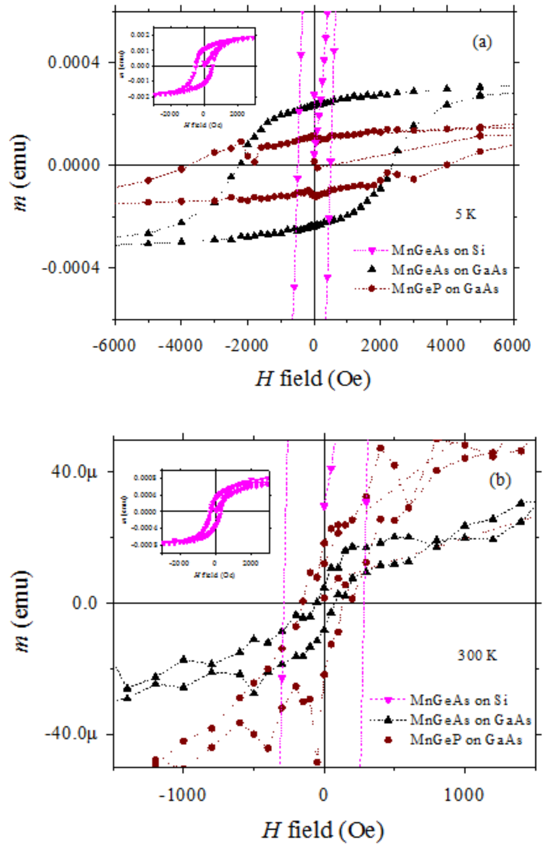

Fig. 4 *M-H* curves for the $MnGeP_2$ and the $MnGeAs_2$ films on GaAs and the $MnGeAs_2$ film on Si at (a) 5 and (b) 300 K. The insets are de-magnified views for the *M-H* curve of the film on Si.

Table 2 Coercive fields of the $MnGeAs_2$ and $MnGeP_2$ films at some temperatures (5 and 300 K for all the samples, 250 K for the films on GaAs) with respect to various growth conditions.

Samples (substrate, growth temperature (^oC))	Coercive Field (Oe)		
	5 K	250 K	300 K
$MnGeAs_2$ (Si(100), 600)	494		286
$MnGeAs_2$ (GaAs(100), 350)	2300	260	70
$MnGeP_2$ (GaAs(100), 350)	3900	1400	160

Magnetoresistance (MR) measurements for the deposited film samples were performed at 5, 305 and 355 K. The MR changes for a $MnGeAs_2$ film in fields between -5 and 5 T, at 5 and 300 K, were found not larger than 9%. Hysteresis in MR curves is clearly seen in the data at 305 K, as shown in Fig. 5(a). The two peak positions, one from a positive sweep of magnetic field (around 1000 Oe) and the other (around -1000 Oe) from a negative sweep, look to be 2000 Oe apart. At 355 K above the transition temperature, no apparent MR change was found. At 5 K, MR changes by very small amount, less than 1%. MR measurement results for a $MnGeP_2$ film are shown in Fig. 5(b). Though MR changes from -5 to 5 T, at 5 and 305 K are small, less than 2%, but hysteresis is clearly seen for both 5 and 305 K data. And no hysteresis was found from the 355 K data, which is above the transition temperature. These results give evidence that some of carriers in the films are spin polarized [18]. When a low magnetic field is applied anti-parallel to the magnetization direction of the sample, two peaks in MR can be usually observed, due to the scattering.

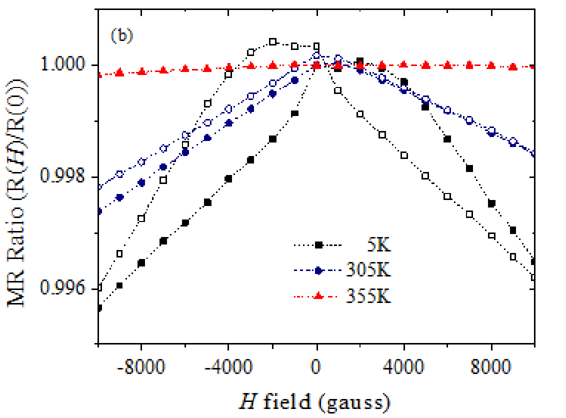

Fig. 5 MR curves for (a) a $MnGeAs_2$ film and (b) a $MnGeP_2$ film on GaAs at 5, 305 and 355 K. All the MR values are normalized with a resistance value at zero field during the sweep-up.

Field dependent Hall resistances have been measured at various temperatures. The anomalous Hall effect in a bar-patterned $MnGeAs_2$ film on GaAs has been observed at temperatures below the FM-PM transition temperature, as shown in Fig. 6(a), indicating the presence of spin polarized carriers in $MnGeAs_2$. At 355 K, above the transition temperature, the ordinary Hall effect was observed and the type of charge carriers have been determined n-type with a effective carrier density is 2×10^{20} cm^{-3}. A $MnGeAs_2$ film was deposited on an p-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 $MnGeAs_2$/p-GaAs system, confirming that the $MnGeAs_2$ film layer is n-type. Hall measurement has also been performed on a patterned $MnGeP_2$ film on GaAs. The anomalous Hall effect was observed in the film at various temperatures from 5 to 305 K below the transition temperature with apparent hysteresis in Hall resistance curve with respect to the magnetic field sweeping direction as shown in Fig. 5(b), and an ordinary Hall effect was viewed at 355 K above the transition temperature, with a p-type (also confirmed from I-V characteristics of a $MnGeP_2$/n-GaAs diode structure) effective carrier density of 6×10^{20} cm^{-3}.

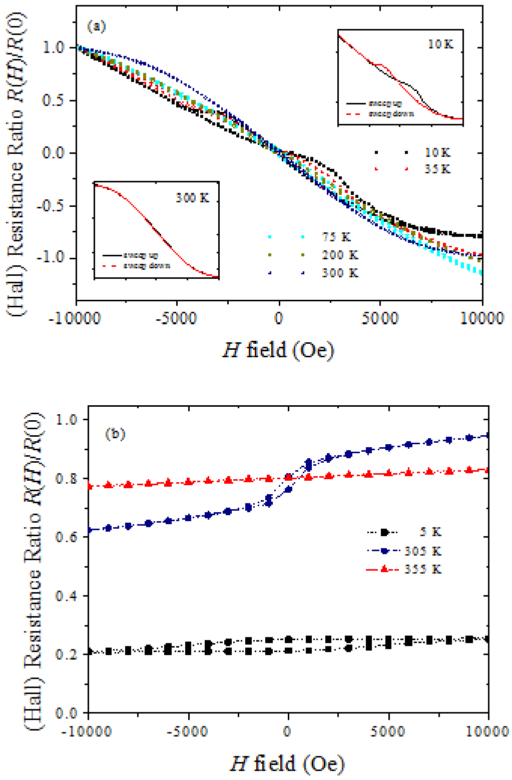

Fig. 6 Hall resistance curves for (a) a $MnGeAs_2$ film and (b) a $MnGeP_2$ film on GaAs at 5, 305 and 355 K. All the Hall resistance values are normalized with a normal zero-field resistance value.

IV. CONCLUSION

$MnGeAs_2$ and $MnGeP_2$ films have been synthesized on GaAs(100) and Si(100) substrates. The films display room-temperature ferromagnetism and a high magnetic moment of 3.4 μ_B and 2.4 μ_B per Mn, respectively. Anomalies in magnetic field dependent transport of the carriers, presumably due to spin polarization were observed from Hall and magnetoresistance measurements. The results of the present investigation suggest that $MnGeAs_2$ and $MnGeP_2$ films are potential candidates for room-temperature spintronic devices.

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