Growth and Magnetic Properties of Chalcopyrite $MnGeAs_2$ Films

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Abstract: *Ferromagnetic $MnGeAs_2$ thin films were grown on GaAs(100) and Si substrates. Magnetization and resistance measurements for $MnGeAs_2$ samples exhibited room-temperature ferromagnetism with TC above 320 K. The coercive fields at 5 and 300 K were obtained. The anomalous Hall effect and hysteresis in magnetoresistance were observed, indicating spin polarization of the n-type carriers in the films. The current-voltage characteristics of a $MnGeAs_2$ film grown on a p-type GaAs substrate displayed semiconducting behavior.*

Keywords: *$MnGeAs_2$, room temperature ferromagnetic semiconductors, chalcopyrite, thin films*

1. INTRODUCTION

Chalcopyrites (II-IV-V2), which are very similar in structure with tetrahedrally-coordinated zinc-blende (III-V) materials, are a class of semiconductors recognized as promising materials for nonlinear optical devices, solar cells, and detectors [1]. The series II-IV-V2 chalcopyrites are all nonmagnetic [2]. However, in Mn-doped chalcopyrites such as $CdGeP_2$ [3], $ZnGeP_2$ [4], and $ZnSnAs_2$ [5] ferromagnetic (FM) orderings were observed near or above room temperature. These ferromagnetic semiconducting materials, with high ferromagnetic transition temperatures and crystal and electronic structures similar to the currently used zinc-blende or pure elemental group IV semiconductor materials, have the potential to advance spintronic devices if their magnetizations are associated large spin polarized carrier densities.

Spin polarized carrier transport is essential to make spin dependent devices such as magnetoresistive (MR) sensor and magnetic tunnel junction [6]. It will be helpful if maturely advanced processing technology in semiconductor industry as well as some useful properties of semiconductors are adapted into the spin dependent devices to reduce the size and enhance the performance. However, known semiconductor materials are nonmagnetic, so that it is not efficient to flow spin polarized current through the semiconductor devices from ferromagnetic metals due to large and rapid spin polarization loss during spin injection between nonmagnetic semiconductors and ferromagnetic metals [7,8]. The occurrence of ferromagnetic semiconductors will solve this problem since it offers an alternate way 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.

Using dilute magnetic semiconductors (DMS) is a strategy to achieve control over the spin degree of freedom [9,10], prepared by substituting magnetically active ions such as V, Cr, Mn, Fe, Co, and Ni into non-magnetic semiconductor hosts. Ferromagnetism has been reported in various classes of semiconductors, II-VI [11], III-V [12,13], and IV [14,15]. The low solubility of magnetic ions in the host semiconductors is limitation to obtain high magnetic moments and high Curie temperatures (T_C).

Here we report the synthesis of the magnetic and electrical transport properties of chalcopyrite semiconducting films of $MnGeAs_2$ on GaAs and Si substrates, with room-temperature ferromagnetism. In $MnGeAs_2$, it is expected that the magnetic 2+ Mn ions occupy all the group II sites (25% of the lattice sites), resulting in a larger magnetization values than diluted magnetic semiconductors.

2. EXPERIMENT

Thin films of $MnGeAs_2$ were deposited on GaAs (001) (a = 5.65315 Å) with a molecular beam epitaxy (MBE) system. GaAs substrates were heated before the deposition upto 600-650 ^{o}C with an arsenic flux to remove surface oxide at GaAs surface and to obtain smooth surface. Then buffer layer of GaAs deposition (50-150 Å) was followed. The deposition rate was maintained to be around 0.5 Å/s. The substrate temperature during the growth was 350 ^{o}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. Streaky RHEED patterns after the buffer deposition and during the film deposition were observed as shown in Fig.'s 1(a) and (b). $MnGeAs_2$ films were also grown on Si(111) and Si(001) (a = 5.4307 Å) substrates. The substrate temperatures were 400-700 °C. RHEED patterns for the films deposited at high substrate temperature were streaky as shown in Fig.'s 1(c) and (d), which are taken from the film sample grown on on Si(111) and at substrate temperature of 700 °C, while those for the films grown at low temperatures were streaky at first then became weaker.

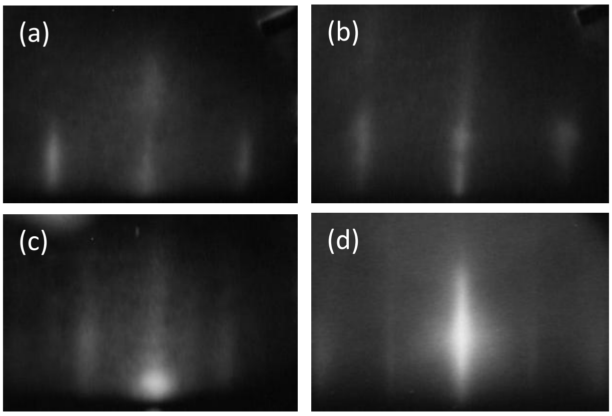
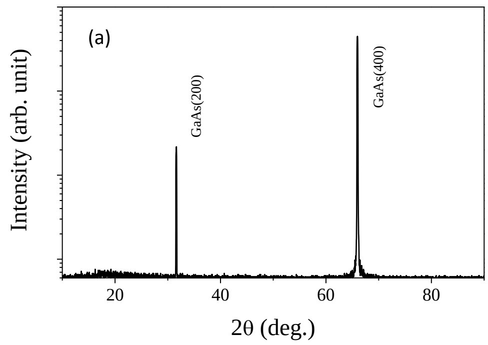


Fig 1: *RHEED images of (a) GaAs(100) substrate before the deposition and of (b) the $MnGeAs_2$ film on GaAs (100) during the deposition. RHEED images of (c) Si(111) substrate before the deposition and of (d) the $MnGeAs_2$ film on Si(111) during the deposition.*

3. RESULTS AND DISCUSSION

The lattice constants for $MnGeAs_2$ are a = 5.782 Å and c = 11.323 Å in bulk [16]. The lattice mismatch between $MnGeAs_2$ and GaAs is 0.1475% (2.25%) (with Si, 6.2657% (4.1611%); hence for our thin $MnGeAs_2$ 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(a). XRD measurements on the films on Si(111) substrates showed several XRD films peaks in the XRD patterns as shown in Fig. 2(b). The highest peaks were (112), and other peaks from the film layers were found small on a log scale plot. Most grains of the film samples seem to grow in (112) oriented, which is reasonable considering that the substrate Si is (111) oriented and the lattice constants of $MnGeAs_2$ are c=2a, and there look to exist some small number of grains with different orientations. Scanning electron microscope (SEM) was used to investigate the morphology of the deposited film samples. SEM images have shown that the thin (less than 1000 Å) layers of $MnGeAs_2$ films on GaAs are flat and smooth. Figure 3 shows SEM images of the films on Si(111) with respect to the substrate temperature. As the substrate temperature increases from 500 to 700 °C, the size of grains of films increases. Energy dispersive x-ray spectroscopy (EDX) measurements were performed on the samples grown on GaAs(100), Si(100) and Si(111) substrates, as summarized in Table 1. From the EDX measurements, the composition of Mn, Ge, and As deviates from stoichiometric value of (1 : 1 : 2), but rather deficient in Mn and abundant in As, as summarized in Table 1. For some samples, inductively coupled plasma atomic emission spectroscopy (ICP-AES) measurement was performed, which revealed that the composition results by EDX for Mn were underestimated and those for As were overestimated. The composition of Mn and As decreases as the substrate (growth) temperature increases, implying that the films deposited at high substrate temperature are Ge rich, so that they can be regarded as alloy films of $MnGeAs_2$ and Ge. Further fine-tuning of the composition will likely be required in achieving device-quality films.



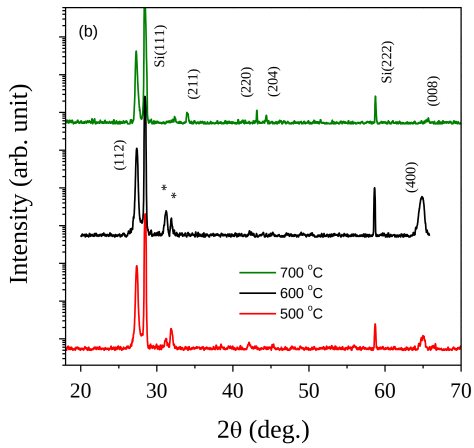


Fig 2: *θ-2θ XRD patterns (a) of a $MnGeAs_2$ film on GaAs(100) substrate and (b) of the $MnGeAs_2$ films on Si(111) substrate, deposited at substrate temperature of 500 (bottom red line), 600 (black line in the middle) and 700 °C (top green line), respectively, on a logarithmic scale. (XRD peaks denoted by * are not well identified with a chalcopyrite structure.)*

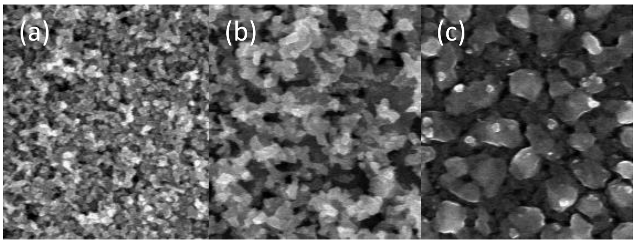


Fig 3: *SEM images of $MnGeAs_2$ films on Si(111) substrate, grown at substrate temperature of (a) 500, (b) 600, and (c) 700 °C, respectively.*

Table 1: *Compositions of Mn, Ge, and As of $MnGeAs_2$ films from EDX measurements (and from ICP-AES measurements in parenthesis) with respect to substrate orientation and growth temperature.*

substrate	temperature (°C)	composition		
		Mn	Ge	As
Si(100)	400	0.96 (2.0)	1	3.7 (2.1)
	550	0.91	1	3.5
	600	0.72	1	2.0
	700	0.43 (1.1)	1	1.1 (0.9)
Si(111)	500	0.46	1	1.7
	600	0.48	1	1.6
	700	0.26 (0.71)	1	0.82 (0.65)

The magnetization of the deposited films was investigated using a Quantum Design SQUID magnetometer. The temperature dependent magnetizations (M) of $MnGeAs_2$ films grown under various growth conditions were measured in a small (500-1000 Oe) external magnetic field (H) between 5 and 400 K, which are shown in Fig. 4(a). The samples show magnetic transitions above room temperature, around 320-360 K. Note that the GaAs substrate is diamagnetic. Field dependent magnetization measurements were also performed the $MnGeAs_2$ film samples at 5 and 300 K. 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 320-360 K are ferromagnetic (FM)-paramagnetic (PM) transition. Among them, *M-H* curves for the film on GaAs(100) at growth temperature 350 °C are shown in Fig. 4 (b). The coercive fields of the $MnGeAs_2$ film at 5, 250, and 300 K are 2300, 260 and 70 Oe, respectively. In Table 2, coercive fields for some of the $MnGeAs_2$ film samples are summarized in Table 2. Film samples grown at lower temperature look to show larger coercive field at 5 K. The magnetic moment per Mn atom at 5 K for the $MnGeAs_2$ film on GaAs was obtained to be 3.4 μB from the saturation magnetization value at 5 K, which is in good agreement with the bulk value [16]. Temperature dependent electrical resistance measurements from 5 to 400 K in zero magnetic field increases with temperature up to the transition temperature and then saturates. The temperature where there is a distinct change, seems to match the FM-PM transition temperature observed in the temperature dependent magnetization measurement. Magnetoresistance (MR) measurements were performed at 5 and 300 K. The MR changes in fields between -5 and 5 T, at 5 and 300 K, were found not larger than 2%. At low magnetic fields, hysteresis in MR measured at lower than transition temperature is apparent. This gives an evidence that some of carriers in the film are spin polarized [17]. When a low magnetic field is applied anti-parallel to the magnetization direction of the sample, two peaks are observed, due to the scattering.

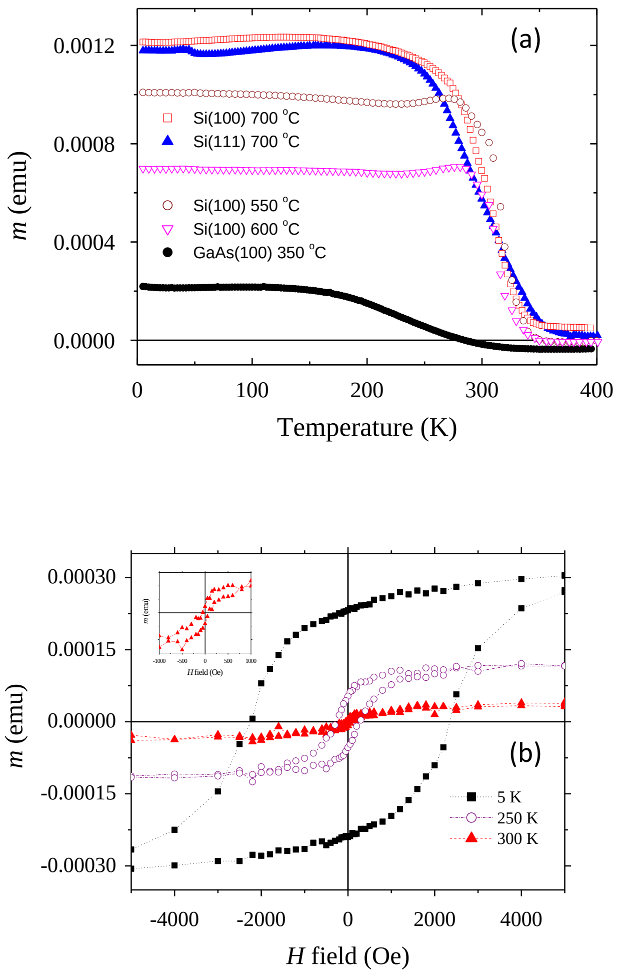


Fig 4: *(a) Temperature dependent magnetization (M) of $MnGeAs_2$ films on GaAs(001), Si(111), and Si(100) substrates. (b) M-H curves for the MnGeP2 film on GaAs(100) at 5, 250, and 300 K. The inset is a magnified view for the M-H curve of the film at 300 K.*

Table 2: *Coercive fields of $MnGeAs_2$ films at some temperatures (5 and 300 K for all the samples, 250 K for a film on GaAs, and 340 K for a film on Si(111)) with respect to various growth condition.*

Substrate	Growth temperature (°C)	Coercive Field (Oe)			
		5K	250K	300K	340K
GaAs(100)	350	2290	260	70	
Si(100)	550	750		380	
	550 (600)	550		310	
	600	490		290	
	700	460		310	
Si(111)	700	240		220	140

Field dependent Hall resistances have been measured at various temperatures. The anomalous Hall effect in a bar-patterned $MnGeAs_2$ film on GaAs(100) has been observed at temperatures below the FM-PM transition temperature, 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 carriers have been determined n-type with the effective carrier density is 2×10^{20} cm^{-3}. A $MnGeAs_2$ film was deposited on an n-type GaAs(100) substrate and the current-voltage (*I-V*) characteristics measured, as shown in Fig. 5. A typical p-n diode type I-V curve is observed for the $MnGeAs_2$/p-GaAs system, indicating that the $MnGeAs_2$ film layer is n-type.

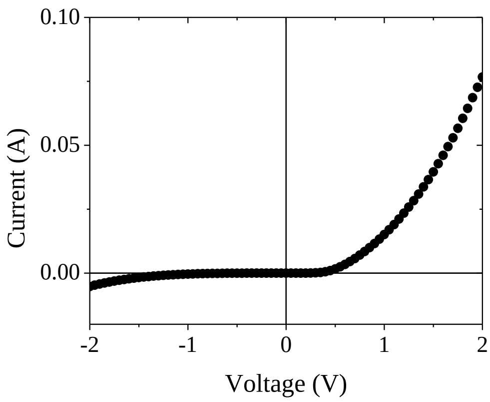


Fig 5: *I-V diode characteristics of a junction between a n-type $MnGeAs_2$ and an p-type GaAs(100) substrate, indicating a semiconducting behavior of the $MnGeAs_2$ film.*

4. CONCLUSIONS

$MnGeAs_2$ films have been synthesized on GaAs(100), Si(100), and Si(111) substrates. The films display room-temperature ferromagnetism and a high magnetic moment of 3.4 μB 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 $MnGeAs_2$ films are potential candidates for room-temperature spintronic devices.

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