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Magnetic and Magneto-Transport Properties of Mn-Doped Germanium Films

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ABSTRACT: *We have successfully fabricated heavily Mn-doped Ge thin films on GaAs and Si substrates. Temperature dependent magnetization and resistance measurements for MnGe film samples exhibited near room-temperature (around 300 K) ferromagnetic ordering mediated possibly by large number of hole carriers in film samples. The coercive fields at 5 K (950-1130 Oe depending on the substrate and the Mn composition) and several other temperatures were obtained. The anomalous Hall effect was observed in a Mn-doped Ge film, suggesting the existence of spin polarized carriers. Mn-doped Ge films showed p-type conduction with the effective carrier densities of* 1×10^{19}*–*5×10^{20} *cm*$^{-3}$ *and the carrier mobilities of 1-10 cm*^{2}*/Vs with respect to Mn composition.*

Keywords: *anomalous Hall effect, magneto resistance, MnGe, room temperature ferromagnetic semiconductors, thin films*

I. INTRODUCTION

The injection of spin polarized carriers into nonmagnetic semiconductors has received enormous interest because it is essential not to advance the existing spintronic devices such as spin-valve and magnetic tunnel junction in performance but also to offer a potential to create new classes of spin-dependent electronic devices. [1] If novel materials with both semiconducting and ferromagnetic features are developed and the fully developed semiconductor processing technology is adapted, new successful spintronic devices will emerge which utilize the correlation between the spin and charge of the carriers with reduced size and enhanced performance. Without ferromagnetic semiconductors, it is not efficient to flow spin polarized current through the semiconductor devices. Spin carrier injection from ferromagnetic metals to nonmagnetic semiconductor is limited due to large and rapid spin polarization loss at the semiconductor-metal interfaces [2,3]. The occurrence of ferromagnetic semiconductors will offer an alternate way to overcome the rapid spin polarization loss. The spin-flip scattering rate at the interface may be reduced in spin injection from a ferromagnetic semiconductor to a lattice and Fermi-level matched nonmagnetic semiconductor.

Dilute magnetic semiconductors (DMS) is a strategy to obtain both semiconducting and magnetic features [4,5], by substituting magnetic ions such as Mn^{2+}, Fe^{2+}, Co^{2+}, and Cr^{2+} into non-magnetic host semiconductors. In semiconductors such as ZnTe, ZnSe, CdTe, and Cd,Se, magnetic ions (2^+) can occupy the cation sites (for group-II) of the host semiconductors, showing antiferromagnetic (AFM) or spin-glass ordering. [6] In III-V compounds, high Curie temperature (T_C ~110K) has been reported for Mn-doped GaAs, where 2^+ Mn ions substitute group III Ga lattice sites and act as acceptors, resulting in a high hole concentration of ~10^{20} cm^{-3}. [7,8] It is generally accepted that these hole carriers may induce the ferromagnetic (FM) ordering. [7-10] In oxide and nitride semiconductors, ferromagnetism in magnetically doped GaN, [11], ZnO, [12] and TiO_2, [13], has been reported with T_C's of 250K, and 280K, and above 400K, respectively. In more complex ternary compounds, FM orderings in Mn-doped chalcopyrites such as $ZnGeP_2$ [14], and $CdGeP_2$ [15], are observed at 312 K and 320 K, respectively.

Here we report the fabrication of Mn-doped Ge films. Magnetic and magneto-electrical transport properties of Mn-doped Ge films on GaAs and Si substrates are presented. Some of film samples have shown FM orderings at near room-temperature.

II. EXPERIMENT

Thin films of Mn-doped Ge were deposited on GaAs (001) (a = 5.65315 Å) and Si (a = 5.4307 Å) with a molecular beam epitaxy (MBE) system. Si and GaAs substrates were heated upto 600 ^{o}C before the deposition (with an As flux for GaAs substrate) to eliminate residual surface oxide or other contaminants after the substrate cleaning process. A GaAs buffer layer deposition (~100 Å) followed for GaAs substrates. For some samples, a Ge buffer layer (~50 Å) was grown before MnGe film deposition. Cell temperature for Ge was varied in a range of 1280-1400 ^{o}C, and that for Mn was varied in a range of 900-1025 ^{o}C. The deposition rate was maintained to be around 0.5 Å/s or less. The substrate temperatures during the growth were 100-550 ^{o}C. To monitor crystal orientation and mode of growth of the deposited film, reflection high-energy electron diffraction (RHEED) was used. Scanning electron microscope (SEM) was used to investigate the morphology of the deposited film samples. Energy dispersive x-ray spectroscopy (EDX) measurement and inductively coupled plasma atomic emission spectroscopy (ICP-AES) measurement were performed on the samples to the composition of film samples. Magnetization measurements at temperatures between 5 and 400 K, at external magnetic field between -5 and 5 T were done on the films samples using a SQUID magnetometer (Quantum Design). Resistance, magnetoresistance, and field dependent Hall measurements were performed on the film samples at various temperatures between 5 and 400 K using a SQUID machine (Quantum Design) with a transport measurement probe.

III. RESULTS AND DISCUSSION

Streaky RHEED patterns after the substrate heating and/or the buffer deposition were observed as shown in Fig.'s 1(a), (c) and (d). During the film deposition, streaky RHEED patterns were observed as shown in Fig.'s 1(b), (d) and (e). In many samples, as the deposition time increases, the RHEED patterns became weaker. The lattice constant for Ge is a = 5.657 Å in bulk (JCPDF No. 04-0545). The lattice mismatch between Ge and GaAs is 0.06806% (and with Si, 4.000%; hence for our thin MnGe layers, we could not resolve the film peaks from the GaAs substrate peaks in x-ray θ-2θ diffraction (XRD) measurements. XRD measurements on MnGe films on Si(100) substrates showed MnGe(200) and (400) peaks in the XRD patterns as shown in Fig. 2. A rocking curve was measured at the MnGe(400) position, showing a broad peak with a full width half maximum of 0.52^{o}. Other peaks from the film layers were not found on a log scale plot. Most grains of the film samples seem to grow in (100) oriented, which is reasonable considering that the substrate Si is (100) oriented.

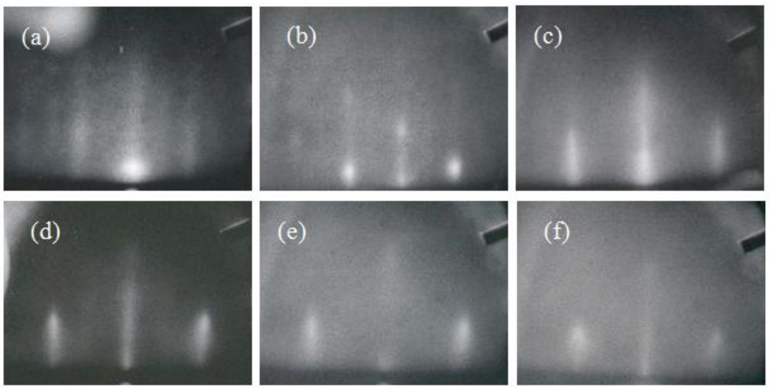

Fig. 1 RHEED images of (a) a Si(100) substrate after preheating and of (b) a Mn_xGe_{1-x} film on Si(100) during the deposition. RHEED images of (c) a GaAs(100) buffer layer, and of (d) a Ge buffer layer on GaAs(100) substrate. RHEED images of a MnGe film during the deposition at substrate temperature of (e) 100 ^{o}C and (f) 550 ^{o}C, respectively.

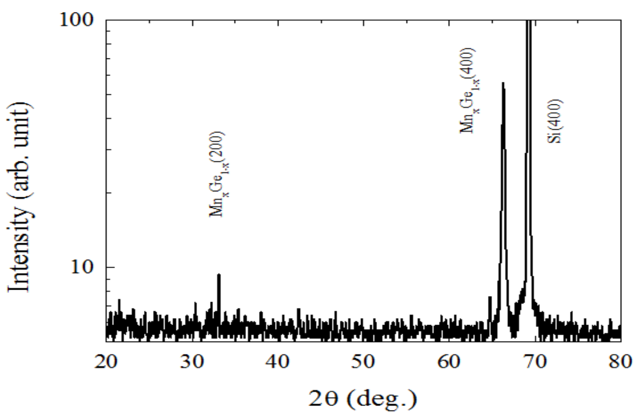

Fig. 2: θ-2θ XRD pattern (a) of a Mn_xGe_{1-x} film on Si(100) substrate.

Scanning electron microscope (SEM) was used to investigate the morphology of the deposited film samples. A SEM image of a MnGe film on Si(100) grown at high substrate temperature of 500 ^{o}C has displayed that the thin layer of Mn_xGe_{1-x} film on Si are flat and smooth, as shown in Fig. 3. The grains of the film look to merge to form large size of grains. Energy dispersive x-ray spectroscopy (EDX) measurements and inductively coupled plasma atomic emission spectroscopy (ICP-AES) measurements were performed on the samples grown on Si(100) and GaAs(100) substrates.

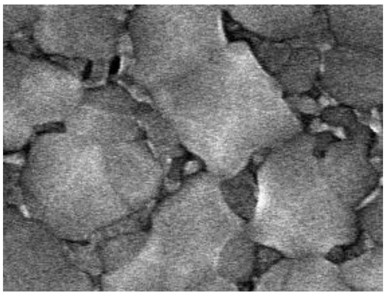

Fig. 3: SEM image of a MnGe film on Si(100) substrate grown at substrate temperature of 500 ^{o}C.

Magnetization measurements performed on the deposited Mn_xGe_{1-x} films using a SQUID magnetometer. Temperature dependent magnetizations (*M*) of Mn_xGe_{1-x} films grown at 500 ^{o}C on GaAs with a Mn composition *x* of 0.049 and Si substrates with *x* of 0.064, respectively, were measured in a small (1000 Oe) external magnetic field (*H*) at temperatures from 5 to 400 K, which are shown in Fig. 4(a). The samples look to show magnetic transitions at two temperatures, one at around 140 K and the other around 300 K. Note that the GaAs substrate is diamagnetic and show negative magnetization values in Mn_xGe_{1-x}/GaAs sample above 260 K. For comparison, data from a bulk Mn_xGe_{1-x} with a Mn composition *x* of 0.06, with two magnetic transitions at 150 and 274 K [16], are shown in the figure. To investigate further on the magnetic transitions, field dependent magnetization measurements were also performed on the Mn_xGe_{1-x} film samples at several temperatures between 5 and 330 K, as shown in Fig.'s 5 (a) and (b). The hysteric ferromagnetic *M-H* curves were observed at 5 K and at temperatures below 330 K, suggesting that the transition around 300 K is ferromagnetic (FM)-paramagnetic (PM) transition. The transition near 150 K in $Mn_{0.06}Ge_{0.94}$ bulk sample [16] is antiferromagnetic (AFM)-ferromagnetic (FM) transition. However, the transition in the Mn_xGe_{1-x} film samples around 140 K does not seem to be a AFM-FM transition, which may be caused by much larger number of carriers in film samples than in bulk samples [17]. The coercive fields of the MnGe film on GaAs at 5, 190, 250 K are 950, 660, and 390 Oe, respectively, while those of the Mn_xGe_{1-x} film on Si at 5, 100, and 210 K are 1130, 340, and 90 Oe, respectively. Temperature dependent electrical resistance measurements from 5 to 400 K in zero magnetic field increases with temperature up to the transition temperature near 140 K and then decreases to 250 K then increases again until 300 K then saturates. The temperature where there are distinct slope changes in the resistance curve, seems to correspond to the transition temperatures observed in the temperature dependent magnetization measurement. These resistance changes at the phase transitions are possibly caused by changes in the spin-flip scattering rates at the magnetic transitions such as FM-PM transition. Compared with magnetization measurement, which can lay emphasis on local effects such as magnetic impurity clusters, resistance data supply an alternate way to investigate the phase transition, which averages over the whole sample. Note that in the second resistance measurement, the resistance curve changed. The curve increases with temperature up to 150 K then decreases until 300 K then saturates, without the resistance increase region from 250 to 300 K.

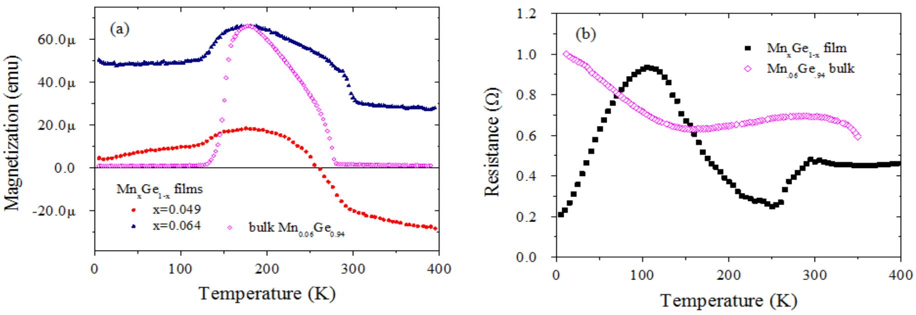

Fig. 4 (a) Temperature dependent magnetization (M) of a $Mn_{0.049}Ge_{0.951}$ film on GaAs and in a $Mn_{0.064}Ge_{0.936}$ film on Si a 1000 Oe magnetic field. The $Mn_{0.06}Ge_{0.94}$ bulk data from reference [16] is plotted for comparison. (b) Temperature dependent resistance of Mn_xGe_{1-x} film under zero magnetic field.

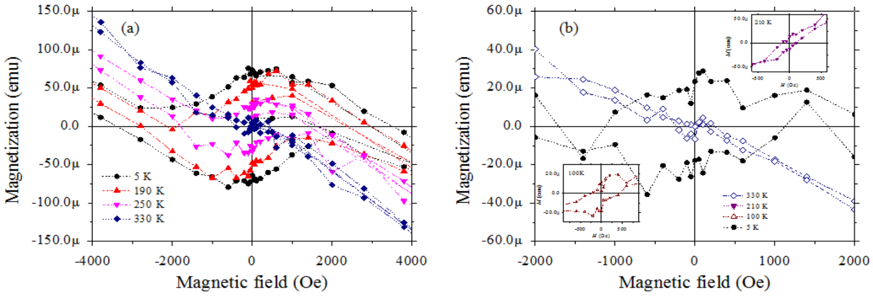

Fig. 5 *M-H* curves (a) for a Mn_xGe_{1-x} film on GaAs at temperatures 5, 190, 250, and 330 K, respectively, and (b) for a Mn_xGe_{1-x} film on Si at temperatures 5, 100, 210 and 330 K, respectively. Data at 100 and 210 K are viewed in the magnified insets.

Temperature dependent resistance (at zero magnetic field) measurements were performed on Mn_xGe_{1-x} films on GaAs grown at substrate temperature of 100 and 550 °C. With the same deposition time and the cell temperatures of Mn and Ge, *i.e.* the same flow rate, the sample grown at low temperature of 100 °C showed semiconducting (decreasing with increasing temperature) behavior while one at high temperature of 550 °C displayed metallic (increasing with increasing temperature). Normalized resistance data are plotted in Fig. 6(a). Magnetoresistance (MR) measurements at 5 and 300 K were also measured for MnGe films grown at 100 and 550 °C. For the sample grown at 100 °C, negative MR was found at 5 K and the maximum MR changes in fields between -2 and 2 T, at 5 K were found to be around 2%, as shown in Fig. 6(b). No MR changes were measured at 300 K. Hysteresis in MR was not clearly seen in this sample. For the sample grown at 550 °C, positive MR was found at 5 K but the maximum MR changes were less than 0.25%, as shown in Fig. 6(c). At 300 K, very small negative MR (less than 0.1% between -2 and 2 T) was found. Field dependent Hall resistances have been measured at various temperatures from 5 to 355 K. The anomalous Hall effect was found in the MnGe film grown at 100 °C, at the measurement temperature of 55 K, as shown in Fig. 6(d). At 105 K and above, anomalous Hall effect was not clearly seen. At 5 K, asymmetric Hall resistance was measured, which can be interpreted due to the MR change (around 2% at 2 T) and the anomalous Hall effect, These results may indicate the presence of spin polarized carriers in MnGe [18]. At high temperatures, the ordinary Hall effect was observed and the carriers have been determined p-type with the effective carrier densities of 1×10^{19}–5×10^{20} cm^{-3} depending on Mn composition, which is much larger than those in bulk Mn_xGe_{1-x} (p-type 9.3×10^{15} cm^{-3} for x = 0.038, p-type 1.9×10^{16} cm^{-3} for x = 0.062, n-type 1.4×10^{16} cm^{-3} for x = 0.013, respectively) [16]. The carrier mobilities were calculated to be 1-10 cm^2/Vs. Pure Ge does not have a net magnetic moment, resulting in diamagnetism [19]. Though in a low Mn concentration Mn_xGe_{1-x} sample, the substituted Mn ions are not closely located to order, resulting in a paramagnetic state, at a higher Mn concentration, long-range ordering can set in, possibly mediated by hole carriers.

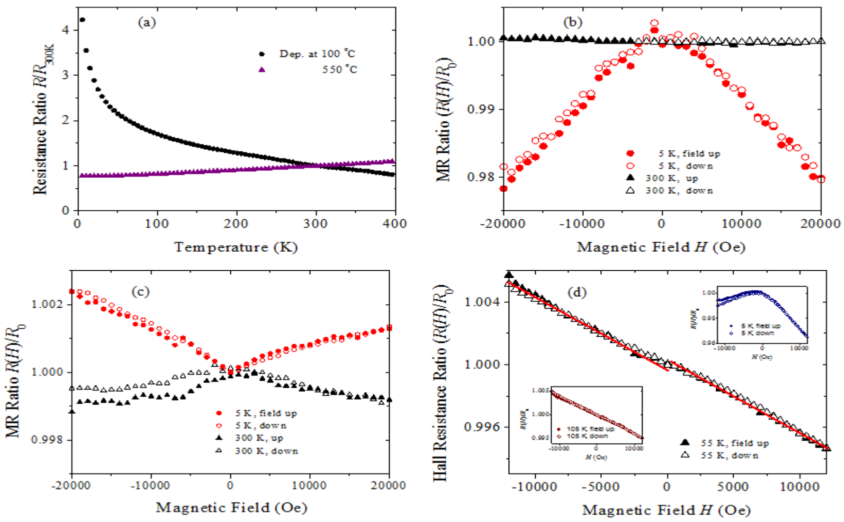

Fig. 6 Resistance curves for (a) Mn_xGe_{1-x} films on GaAs grown at 100 and 550 °C. Magnetoresistance curves (normalized with a zero field resistance value) of a Mn_xGe_{1-x} film grown at 100 °C, and (c) of a Mn_xGe_{1-x} film, at 550 °C at 5 and 300 K. (d) Normalized Hall resistance values at 5, 55 and 105 K for a Mn_xGe_{1-x} film grown at 100 °C.

IV. CONCLUSION

In conclusion, we have synthesized Mn-doped Ge thin films on GaAs and Si substrates. Mn_xGe_{1-x} film samples exhibited near room-temperature (around 300 K) ferromagnetic ordering mediated possibly by large number of hole carriers in film samples. Ferromagnetic hysteresis was found in Mn_xGe_{1-x} films at 5K with coercive fields of 950-1130 Oe depending on the substrate and the Mn composition. The anomalous Hall effect was observed in a Mn-doped Ge film, suggesting the existence of spin polarized carriers. Mn-doped Ge films showed p-type conduction with the effective carrier densities of 1×10^{19}–5×10^{20} cm^{-3} and the carrier mobilities of 1-10 cm^2/Vs with Mn composition. These results may open a way to utilize ferromagnetism in group IV elemental semiconductors. Ferromagnetic transition above room-temperature might be possible with additional doping, as observed in other dilute magnetic semiconductors.

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