Carrier-induced ferromagnetism in Ge$_{0.92}$Mn$_{0.08}$Te epilayers with a Curie temperature up to 190 K

Y. Fukuma$^{1,a}$, H. Asada$^2$, S. Miyawaki$^2$, T. Koyanagi$^2$, S. Senba$^3$, K. Goto$^3$, and H. Sato$^4$

$^1$Yamaguchi Prefectural Industrial Technology Institute, 4-1 Asutopia, Ube 755-0195, Japan
$^2$Department of Material Science and Engineering, Graduate School of Science and Engineering, Yamaguchi University, 2-16-1 Tokiwadai, Ube 755-8611, Japan
$^3$Ube National College of Technology, 2-14-1 Tokiwadai, Ube 755-8555, Japan
$^4$Hiroshima Synchrotron Radiation Center, Hiroshima University, 2-313 Kagamiyama, Higashi-Hiroshima 739-8526, Japan

(Received 21 May 2008; accepted 20 November 2008; published online 22 December 2008)

IV-VI diluted magnetic semiconductor Ge$_{0.92}$Mn$_{0.08}$Te epilayers are grown on BaF$_2$ substrates by molecular beam epitaxy. The ferromagnetic behaviors, such as the spontaneous magnetization, the coercive field, and the Curie temperature $T_C$, are altered by the hole concentration $p$. In the Ge$_{0.92}$Mn$_{0.08}$Te layer with high $p$, strong magnetic anisotropy and the temperature dependence of the magnetization expected for homogeneous ferromagnets are observed, implying that long-range ordering is induced by the holes. The maximum $T_C$ reaches 190 K for $p=1.57 \times 10^{21}$ cm$^{-3}$, which is the highest value for carrier-induced ferromagnetism in DMSs.

The Ge$_{1-x}$Mn$_x$Te layers were grown on BaF$_2$ (111) substrates by MBE. Prior to the growth, the BaF$_2$ substrates were preheated at 600 °C for 30 min. A 30 nm GeTe buffer layer was grown at 350 °C using a GeTe compound effusion cell. For the growth of Ge$_{1-x}$Mn$_x$Te, additional Mn and Te$_2$ effusion cells were used. The beam flux rate was measured by an ion gauge flux monitor. Following the GeTe growth, a Ge$_{1-x}$Mn$_x$Te layer was grown at substrate temperatures $T_S$ ranging from 200 to 350 °C and with a Te$_2$/Mn flux ratio ranging from 2 to 10. The hole concentration was controlled by the growth condition because bulk GeTe has a nonstoichiometric composition with Ge vacancies, which act as a doubly charged acceptor. Higher $T_S$ while supplying enough Te$_2$ flux prevents formation of the nonstoichiometric defects and thus leads to lower $p$. On the other hand, low $T_S$ causes degradation of the crystallinity of the Ge$_{1-x}$Mn$_x$Te layer, causing an increase in $p$, as will be discussed later. The thickness of the Ge$_{1-x}$Mn$_x$Te layer is 300–500 nm, and the growth rate was 0.6–1.0 μm/h. Reflective high-energy electron diffraction (RHEED) was used in situ to study the growth of Ge$_{1-x}$Mn$_x$Te. Figure 1 shows RHEED patterns along the [110] azimuth for (a) Ge$_{1-x}$Mn$_x$Te layer grown at $T_S=350$ °C and Te$_2$/Mn=10 (W060), and (b) Ge$_{1-x}$Mn$_x$Te layer grown at $T_S=250$ °C and Te$_2$/Mn=2 (W069). A well resolved sharp streaky pattern is observed for W060, implying a two-dimensional growth mode. For W069, while the RHEED shows a broad pattern, the pattern retains the characteristic feature of the rocksalt structure. The x-ray diffraction (XRD) patterns of the Ge$_{1-x}$Mn$_x$Te layers are shown in Fig. 1(c). The peak intensity of the (222) peak for W069 decreases drastically, implying the degradation of the crys-
talline quality of the Ge$_{1-x}$Mn$_x$Te layer grown at low temperatures. For W069, many stacking faults were observed along the film plane in the transmission electron microscope measurements. However, the selected area diffraction was found to be only rocksalt Ge$_{1-x}$Mn$_x$Te and there was no indication of the formation of second phases. The Mn composition determined by electron probe microanalysis was $x \sim 0.08$ for all the samples studied here, while the XRD peak position of the Ge$_{1-x}$Mn$_x$Te layer is shifted. The lattice constant $a$ deduced from the (222) peak position was 0.603 and 0.609 nm for W060 and W069, respectively, which are larger than that for bulk ($x = 0.1$, $a = 0.596$ nm, $\alpha = 88.83\%$). The hole concentration $p$ determined by Hall measurement at room temperature was 2.82 $\times 10^{20}$ and $1.75 $ $\times 10^{21}$ cm$^{-3}$ for W060 and W069, respectively.

To check the local electronic structure of Mn ions into GeTe, photoemission spectroscopy (PES) using hard x rays (HX) ($h\nu \sim 7$ keV) was performed. The HX-PES experiments were carried out at the undulator beam line BL47XU of SPring-8. Figure 1(d) shows the Mn 2$p$ core-level spectra at room temperature. A carbon cap layer was deposited in situ to prevent the contamination of the surface of the Ge$_{0.92}$Mn$_{0.08}$Te layer. The measurements were done on the surface without sputtering because of a large escape depth from the surface at high energy (above 5 nm at 6 keV). The spectra show a spin-orbital doublet ($\sim 640$ and 651 eV) with a charge-transfer satellite ($\sim 645$ and 658 eV), implying the nearly localized Mn$^{2+}$ 3$d$ state. The peak positions of the Mn 2$p$ spectra are the same for all the layers. Therefore, the Mn ions are randomly substituted for the cation sites in the host GeTe lattice and the local chemical state of Mn ions is identical for all the Ge$_{1-x}$Mn$_x$Te layers.

The magnetization measurements were done by a superconducting quantum interference device (SQUID) magnetometer. Figures 2(a) and 2(b) show the magnetization curves at 5 K for W060 and W069, respectively. As $p$ increases, the spontaneous magnetization and the magnetic anisotropy are drastically enhanced. The strong magnetic anisotropy could be attributed to a large orbital magnetic moment for Ge$_{1-x}$Mn$_x$Te, in which the Te 5$p$ electron transfer mainly to the $t_{2g}$ state of Mn ions in the $O_h$ symmetry. Figure 2(c) shows the temperature dependence of the magnetization ($M$-$T$) at 500 Oe. A concave $M$-$T$ behavior is observed for W060, implying a short-range ferromagnetic order due to a lack of the hole concentration enough to generate a uniform ferromagnetism. On the other hand, for W069, the $T^{3/2}$ dependence expected for a homogeneous ferromagnet is observed. While high $T_C$ ferromagnetism has been so far reported for various semiconductors, the nonsquareness hysteresis loop with a small magnetic moment and concavity in the $M$-$T$ curve imply a short-range ferromagnetic order. A nonuniformity of the crystallinity may cause such a short-range ordering by a localization of carriers and aggregation of magnetic ions. In the case of W069, while the crystallinity is degraded by the low-temperature growth, the strong magnetic anisotropy and the $T^{3/2}$ dependence in the $M$-$T$ curve indicate that the ferromagnetic ordering is of long-range type. The crystalline defects increase $p$ and thus the ferromagnetism can be enhanced via the Ruderman–Kittel–Kasuya–Yosida (RKKY) interaction. $T_C$, determined by the extrapolation of the main part of the $M$-$T$ curves as denoted by the arrows in Fig. 2(c), is 130 and 190 K for W060 and W069, respectively. $T_C$ is significantly higher than that of previous studies at similar $x$ ($T_C \sim 20$ K).

In the magnetotransport measurements, a negative magnetoresistance with a hysteresis loop and a clear anomalous
Hall effect were observed below $T_C$, as reported for Ge$_{0.6}$Mn$_{0.4}$Te.\textsuperscript{26,27} Figure 3 shows the dependence of anomalous Hall term $R_M$, the coercive field $H_C$, and $T_C$ on the hole concentration for Ge$_{0.92}$Mn$_{0.08}$Te layers. The ferromagnetic order increases with increasing $p$, then exhibits a saturation for $\sim 3 \times 10^{21}$ cm$^{-3}$ and starts to decrease as $p$ further increases. The maximum $T_C$ is 190 K for $p=1.57 \times 10^{21}$ cm$^{-3}$. The decrease in the ferromagnetic order in the high $p$ region could be due to the damping effect of the exponential factor within the RKKY mechanism, as observed in Pb$_{1-x}$Sn$_x$Te.\textsuperscript{10}

In summary, we have grown the IV-VI DMS Ge$_{0.92}$Mn$_{0.08}$Te layer on BaF$_2$ (111) substrates by MBE. A $T_C$ of 190 K ($x \sim 0.08$) is the highest value for carrier-induced ferromagnetism in DMSs. Further increase in $T_C$ might be expected by increasing the Mn composition because the solubility limit of Mn into GeTe is quite high ($x \sim 0.96$).\textsuperscript{11} The Ge$_{1-x}$Mn$_x$Te layer, therefore, offers an interesting opportunity to study novel devices utilizing carrier-induced ferromagnetism, as well as added spin-polarized states in IV-VI heterostructures.

The authors thank K. Kobayashi, and E. Ikenaga for the help with the HX-PES measurements and T. Matsushita, S. Otabe, and M. Kiuchi for the help with the SQUID measurements. The experiments at SPring-8 were performed under the approval of the Japan Synchrotron Radiation Research Institute (Proposal No. 2005B0188).

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{figure3.png}
\caption{(Color online) Hole concentration dependence of (a) anomalous Hall term and coercive field at 15 K (b) $T_C$ for Ge$_{0.92}$Mn$_{0.08}$Te. Lines are guide for the eyes.}
\end{figure}