Growth of Ferromagnetic Semiconducting Si:Mn Film by Vacuum Evaporation Method

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Nowadays, diluted magnetic semiconductors (DMSs) have been widely studied, especially for the III−V and II−VI compound semiconductors.[1−3] We have interested group IV-based DMS, which is a promising material, especially for microelectronics applications. Park et al. reported on the epitaxial growth of a Mn_xGe_{1-x}, in which the Curie temperature is found to increase linearly with manganese (Mn) concentration from 25 to 116 K, by molecular beam epitaxy (MBE).[4] Gajdzik et al. reported on the ferromagnetism in Mn/C/Si triple layers above room temperature.[5] Recently, Yokoda et al. reported the fabrication of single-phase $Si_{0.997}Ce_{0.003}$ films and their magnetic and electrical transport properties, and also examine the annealing effects, which vary the crystallographic state of the host Si and the coordination of Ce.[6] Here, we demonstrate the growth of ferromagnetic semiconducting $Si_{1-x}Mn_x$ film by vacuum evaporation and the investigation of magnetic and electrical properties of $Si_{0.93}Mn_{0.07}$ film.

The $Si_{1-x}Mn_x$ films were deposited by vacuum evaporation on (111) Si substrates. The deposition rates of Si and Mn were measured using a thickness monitor. The thickness of the sample was fixed at 2 μm. These $Si_{1-x}Mn_x$ films were characterized by energy-dispersive spectroscopy (EDS), X-ray diffraction (XRD), a superconducting quantum interface device magnetometer (SQUID), and temperature dependence of resistivity ($\rho-T$).

The XRD patterns of the as-deposited Si:Mn film show that the film was amorphous (not shown here). The selective area electron diffraction (SAED) pattern (Figure 1a) also suggests that the film was amorphous without any precipitation of silicides and other components in the crystalline phase. To crystallize the film, samples were annealed at 773−1173 K for 1 min in a vacuum ($\sim10^{-3}$ Torr) by a rapid thermal annealing (RTA) system. Figure 1b shows the XRD pattern of the sample annealed at 973 K. The $Si_{1-x}Mn_x$ related peak shows a shoulder at the lower angle side of (111) Si substrate diffraction (inset in Figure 1b). The lattice constant of $Si_{1-x}Mn_x$ increases with Mn concentration, which is due to the larger Mn atomic radius (1.79 Å) compared with that of Si (1.46 Å). The diffraction intensity of the shoulder, which was identified as that of the film, is hundreds of times as large as the expected diffraction intensity of a polycrystalline film, leading us to conclude that the film consists of epitaxially grown Si and a very small amount of poly-Si. A detailed cross-sectional TEM analysis has revealed that polycrystalline Si exists near the surface of the film (not shown here). Since the polycrystalline region could be removed by chemical etching, all the experiments subsequently discussed were performed using the sample etched off the surface layer. No silicide precipitation has been recognized in the annealed sample, even by SAED observation.

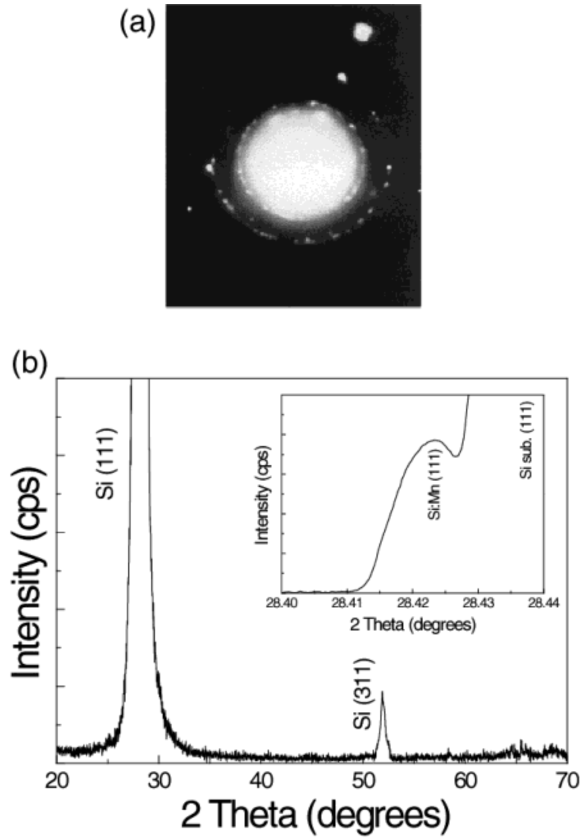

Figure 1. Selective area electron diffraction (SAED) pattern of the as-deposited Si:Mn film and X-ray diffraction pattern of the Si:Mn film after annealing. Inset shows the narrow scan around Si (111).

Figure 2 shows the temperature-dependent magnetization ($M-T$) measured in an applied field of 3 kOe of the sample annealed at 973 K. The onset of ferromagnetism is seen at $T_c = 210 \pm 5$ K with the error arising from the uncertainty of subtracting the Curie−Weiss tail above T_c. Because there is no silicide precipitation in the annealed sample, this magnetization

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(1) Munekata, H.; Ohno, H.; Molnar, S. von; Segmuller, A.; Chang, L. L.; Esaki, L. *Phys. Rev. Lett.* **1989**, *63*, 1849.
(2) Furdyna, J. K.; Kossut, J. *Diluted Magnetic Semiconductors, Semiconductors and Semimetals*; Academic: New York, 1998; Vol. 125.
(3) Geschwind, S.; Ogielski, A. T.; Devlin, G.; Hegarty, *Jpn. J. Appl. Phys.* **1988**, *63*, 329.
(4) Park, Y. D.; Hanbicki, A. T.; Erwin, S. C.; Hellberg, C. S.; Sullivan, J. M.; Mattson, J. E.; Ambrose, T. F.; Wilson, A.; Sapnos, G.; Jonker, B. T. *Science* **2002**, *295*, 651.
(5) Gajdzik, M.; Sürgers, C.; Kelemen, M. Hillebrands, B.; Löhneysen, H. v. *Appl. Phys. Lett.* **1996**, *68*, 3189.
(6) Yokoda, T.; Fujimura, M.; Ito, T. *Appl. Phys. Lett.* **2002**, *81*, 4023.

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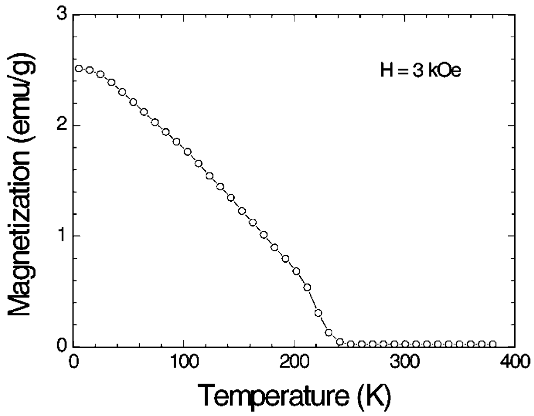

Figure 2. Magnetization (M) vs temperature (T) for a $Si_{0.93}Mn_{0.07}$ film in an applied field $H = 3$ kOe.

is purely from DMS. The possible origin of ferromagnetism in this system is understood to be similar to other group IV magnetic semiconductors.[4,7,8] The long-range Ruderman−Kittel−Kasuya−Yoshida (RKKY) interaction between localized Mn spins and the carrier-mediated spin−spin interaction[9] are considered at the same time. Besides these, the disorder of Mn site locations[10] and double-resonance mechanism[11] are discussed as the origin of the ferromagnetism of III−V magnetic semiconductors.

Figure 3 shows three magnetization curves taken at 5, 100, and 200 K after subtraction of the diamagnetic contribution of the Si substrate. It shows clear temperature dependence of hysteresis. The coercive field decreases monotonically with increasing temperature. For our samples, the coercive fields, H_c, are 320, 150, and 70 Oe at 5, 100, and 200 K, respectively. Magnetization was measured up to 3 kOe without evidence of an increase of magnetization beyond the value acquired in 3 kOe. In this study, the saturation magnetizations, M_s, are 2.43, 1.78, and 0.67 emu/g at 5, 100, and 200 K, respectively.

Figure 4 shows the resistivity change versus the inverse temperature of the sample annealed at 973 K. The temperature dependence of resistivity was measured in the temperature range from 5 to 350 K. The resistivity increases with decreasing temperature according to $\rho = \rho_0 \exp(E_a/kT)$, as is usually found for thermally activated conduction processes having an activation energy of E_a.[6] The resistivity exponentially decreases from 210 ± 5 K with an increasing temperature.

In conclusion, we have fabricated $Si_{0.93}Mn_{0.07}$ film at very low temperature (673 K) by vacuum evaporation, which is ferromagnetic with a well-defined Curie temperature of 210 ± 5 K. The as-deposited film was amorphous; however, the film epitaxially crystallizes by annealing at 973 K. For this sample, the coercive field decreases monotonically with increasing temperature.

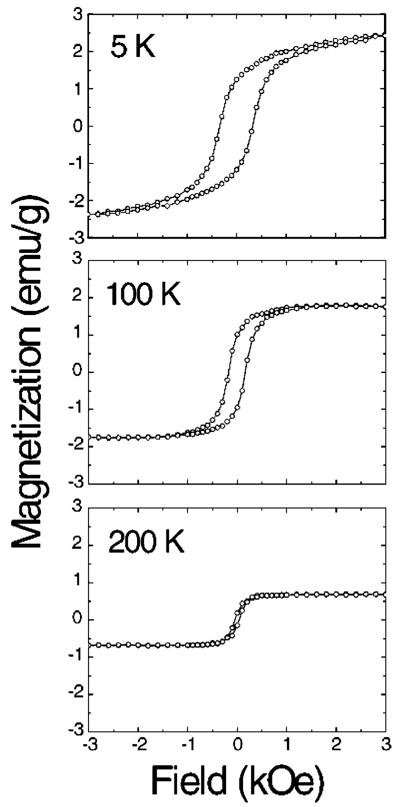

Figure 3. Magnetization vs magnetic field curves ($M-T$) of a $Si_{0.93}Mn_{0.07}$ film for different measuring temperatures (T).

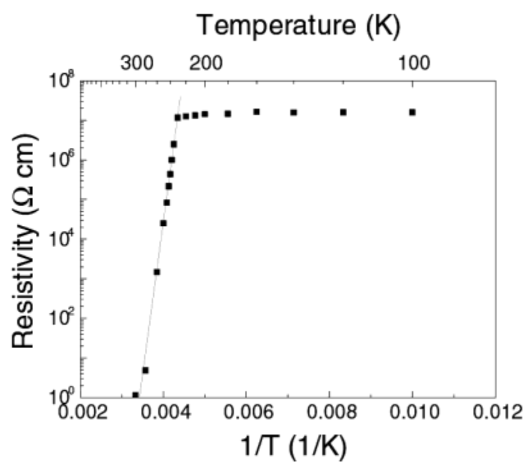

Figure 4. Temperature dependence of resistivity ($\rho-T$) for annealed $Si_{0.93}Mn_{0.07}$ film annealed at 973 K.

The coercive fields, H_c, are 320, 150, and 70 Oe at 5, 100, and 200 K, respectively, and the saturation magnetizations, M_s, are 2.43, 1.78, and 0.67 emu/g at 5, 100, and 200 K, respectively. The resistivity decreases as the temperature increases in the $Si_{0.93}Mn_{0.07}$ film. The temperature dependence of resistivity shows a normal semiconductor property.

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Supporting Information Available: All figures for the properties of Si:Mn film in this paper (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) Zhao, Y.-J.; Shishidou, T.; Freeman, A. J. *Phys. Rev. Lett.* **2003**, *90*, 047204.
(8) Cho, S.; Choi, S.; Hong, S. C.; Kim, Y.; Ketterson, J. B.; Kim, B.-J.; Kim. Y. C. *Phys. Rev. B* **2002**, *66*, 033303.
(9) Dietl, T.; Haury, A.; d'Aunigne, Y. M. *Phys. Rev. B* **1997**, *55*, R3347.
(10) Korzhavyi, P. A.; Abrikosov, I. A.; Smirnova, E. A.; Bergqvist, L.; Mohn, P.; Mathieu, R.; Svedlindh, P.; Sadowski, J.; Isaev, E. I.; Vekilov, Yu. Kh.; Eriksson, O. *Phys. Rev. Lett.* **2002**, *88*, 187202.
(11) Inoue, J.; Nonoyama, S.; Itoh, H. *Phys. Rev. Lett.* **2000**, *287*, 1019.